

SYNTHESIS AND STRUCTURE OF GOLD COMPLEXES [*p*-Tol₄Sb][*p*-TolAuCl₃] AND [*p*-Tol₄Sb][AuCl₄]

V.V. Sharutin, vvsharutin@rambler.ru

O.K. Sharutina, sharutinao@mail.ru

V.S. Senchurin, senvl@rambler.ru

South Ural State University, Chelyabinsk, Russian Federation

Gold complexes [*p*-Tol₄Sb]⁺[*p*-TolAuCl₃]⁻ (**1**) and [*p*-Tol₄Sb]⁺[AuCl₄]⁻ (**2**) have been synthesized by interaction of tetra-*para*-tolylstibonium chloride and aurichlorohydric acid tetrahydrate in acetone. In **1** the tetra-*para*-tolylstibonium cations are tetrahedral (Sb-C 2.091(7)-2.097(6) Å, CSbC 106.1(3)^o-112.7(3)^o), the [*p*-TolAuCl₃]⁻ anions have square-planar structure (Au-Cl 2.286(2)-2.389(2) Å, Au-C 2.028(7) Å, ClAuCl 89.92(9)^o, 92.42(9)^o, 176.68(8)^o, CAuCl 88.27(18)^o, 89.57(18)^o, 175.59(19)^o). In crystal **2** the geometrical characteristics of cations (Sb-C 2.076(7)-2.097(9), CSbC 106.5(3)^o-111.5(4)^o) and [AuCl₄]⁻ square-planar anions (Au-Cl 2.248(3)-2.278(3) Å, ClAuCl 89.17(9)^o-90.74(13)^o, 177.24(16)^o, 177.61(13)^o) are similar to those in **1**.

Keywords: synthesis, structure, gold compounds, X-ray diffraction analysis.

Introduction

Synthesis and structure of complex compounds of gold, containing [AuHal₄]⁻ anions in their composition, were mentioned in the literature [1-5]. In the present paper the synthesis and structure of gold complexes [*p*-Tol₄Sb][AuCl₄] and [*p*-Tol₄Sb][*p*-TolAuCl₃] are described.

Experimental

Synthesis of [*p*-Tol₄Sb]⁺[*p*-TolAuCl₃]⁻ (1**).** Tetra-*para*-tolylantimony chloride 0.250 g (0.48 mmol) and aurichlorohydric acid tetrahydrate 0.197 g (0.48 mmol) were dissolved in 10 mL acetone, then 5 mL toluene was added. The solution was left to stand for 12 h at 20 °C. After evaporation of the solvent 0.287 g (68%) of tetra-*para*-tolylantimony *para*-tolyltrichloroaurate was obtained (mp 156 °C). IR spectrum (ν, cm⁻¹): 484, 587, 800, 1007, 1072, 1194, 1305, 1401, 1492, 1588, 1627, 1905, 2926. Found, %: C 47.38, H 4.03. Calculated for C₃₅H₃₅AuCl₃, %: C 47.72, H 3.98.

Synthesis of [*p*-Tol₄Sb]⁺[AuCl₄]⁻ (2**).** a) The mixture of tetra-*para*-tolylantimony chloride 0.137 g (0.26 mmol) and aurichlorohydric acid tetrahydrate 0.108 g (0.26 mmol) in 10 mL acetone stood for 24 h at room temperature. The solvent was evaporated. The yield is 0.205 g (95%) of tetra-*para*-tolylantimony tetra-*para*-chloroaurate with decomposition temperature 148–150 °C. IR spectrum (ν, cm⁻¹): 483, 529, 585, 633, 697, 809, 1101, 1040, 1066, 1123, 1190, 1212, 1313, 1396, 1444, 1493, 1589, 1708, 2863, 2918, 2953, 3045. Found, %: C 40.52, H 3.49. Calculated for C₂₈H₂₈SbAuCl₄, %: C 40.75, H 3.40.

b) The mixture of penta-*para*-tolylantimony 0.181 g (0.31 mmol) and aurichloric acid tetrahydrate 0.129 g (0.31 mmol) in 10 mL acetone stood for 24 h at room temperature. The solvent was evaporated. The yield is 0.232 g (90%) of pale yellow tetra-*para*-tolylantimony tetrachloroaurate, the melting point and IR spectrum coincide with tetra-*para*-tolylantimony tetrachloroaurate obtained according to method a. Found: %: C 40.54, H 3.52. Calculated for C₂₈H₂₈SbAuCl₄, %: C 40.75, H 3.40.

IR spectra were recorded on the Bruker Tensor 27 in KBr pellets.

The X-ray diffraction analyses of crystals **1** and **2** were 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 *SAINTE-Plus* programs [6]. All calculations for structure determination and refinement were performed using the *SHELXL/PC* programs [7]. The structures were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms.

The main crystallographic data and refinement results for the structures are listed in Table 1. The selected bond lengths and bond angles are given in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1000139 for **1**, CCDC 1000140 for **2**; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Table 1
Crystallographic data, the experimental and structure refinement parameters for compounds **1**, **2**

Parameter	Value	
	1	2
<i>M</i>	880.70	825.02
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /n
<i>a</i> , Å	12.748(5)	12.7962(5)
<i>b</i> , Å	14.941(5)	14.8701(5)
<i>c</i> , Å	18.19 8(10)	16.1167(5)
α, град	90.00	90.00
β, град	102.87(4)	101.8270(10)
γ, град	90.00	90.00
<i>V</i> , Å ³	3379(3)	3001.59(18)
<i>Z</i>	4	4
ρ(calcd.), г/см ³	1.731	1.826
μ, мм ⁻¹	5.395	6.153
<i>F</i> (000)	1704.0	1576.0
Crystal size, mm	0.54 × 0.36 × 0.34	0.99 × 0.61 × 0.5
2θ Range of data collection, deg	4.48 – 62.1°	6.16 – 60.1°
Range of refraction indices	-18 ≤ h ≤ 18, -16 ≤ k ≤ 21, -25 ≤ l ≤ 26	-17 ≤ h ≤ 13, -20 ≤ k ≤ 7, -22 ≤ l ≤ 20
Measured reflections	38599	7733
Independent reflections	10659 (R _{int} = 0.0819)	5051 (R _{int} = 0.0298)
Refinement variables	366	311
GOOF	1.011	0.993
<i>R</i> -factors for F ² > 2σ(F ²)	R ₁ = 0.0653, wR ₂ = 0.1145	R ₁ = 0.0416, wR ₂ = 0.0913
<i>R</i> -factors for all reflections	R ₁ = 0.1352, wR ₂ = 0.1342	R ₁ = 0.1046, wR ₂ = 0.1137
Residual electron density (min/max), e/Å ³	2.06/-0.82	0.55/-0.85

Table 2
Selected bond lengths (*d*) and bond angles (ω) in the structures of compounds **1**, **2**

Bond <i>d</i> , Å		Angle ω, deg	
1			
Au(1)–Cl(1)	2.286(2)	Cl(1)Au(1)Cl(2)	176.68(8)
Au(1)–Cl(2)	2.292(2)	C(41)Au(1)Cl(3)	175.59(19)
Au(1)–Cl(3)	2.389(2)	C(1)Sb(1)C1(1)	110.6(3)
Au(1)–C(41)	2.028(7)	C(1)Sb(1)C(21)	106.1(3)
Sb(1)–C(1)	2.094(6)	C(21)Sb(1)C(11)	112.7(3)
Sb(1)–C(11)	2.097(6)	C(31)Sb(1)C(1)	111.3(3)
Sb(1)–C(21)	2.095(7)	C(31)Sb(1)C(11)	108.1(3)
Sb(1)–C(31)	2.091(7)	C(31)Sb(1)C(21)	108.0(3)
2			
Au(1)–Cl(1)	2.266(3)	Cl(1)Au(1)Cl(2)	90.74(13)
Au(1)–Cl(2)	2.269(3)	Cl(1)Au(1)Cl(3)	89.58(13)
Au(1)–Cl(3)	2.278(3)	Cl(2)Au(1)Cl(3)	177.61(13)
Au(1)–Cl(4)	2.248(3)	Cl(4)Au(1)Cl(1)	177.24(16)

Bond <i>d</i> , Å		Angle ω , deg	
Sb(1)–C(1)	2.076(9)	Cl(4)Au(1)Cl(2)	89.17(13)
Sb(1)–C(11)	2.095(8)	Cl(4)Au(1)Cl(3)	90.62(13)
Sb(1)–C(31)	2.097(9)	C(1)Sb(1)C(1)	109.5(3)
Sb(1)–C(21)	2.086(8)	C(1)Sb(1)C(31)	111.5(4)
C(1)–C(2)	1.391(13)	C(1)Sb(1)C(21)	109.4(3)
C(1)–C(7)	1.370(12)	C(11)Sb(1)C(31)	106.5(3)
C(2)–C(3)	1.375(16)	C(21)Sb(1)C(11)	111.2(3)
C(4)–C(5)	1.501(16)	C(21)Sb(1)C(31)	108.6(4)

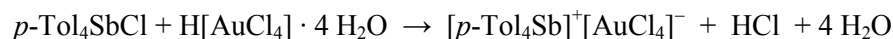
Results and Discussion

It is known that the product of pentaphenylantimony reaction with aurichlorohydric acid (hydrogen tetrachloroaurate (III)) at 20 °C in acetone is tetraphenylantimony tetrachloroaurate, separated from the reaction mixture with 84 % yield [2].

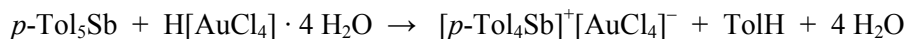
We have found that in similar conditions the interaction of aurichlorohydric acid, obtained by dissolving jewelry gold in aqua regis, with tetra-*para*-tolylantimony chloride runs with formation of tetra-*para*-tolylantimony *para*-tolyltrichloroaurate (1):



If chemically pure aurichlorohydric acid is used, such an unusual transmetalation reaction between antimony and gold compounds is not observed. In this case the formation of tetra-*para*-tolylantimony tetrachloroaurate (2) occurs:



Complex 2 has also been obtained from penta-*para*-tolylantimony and aurichlorohydric acid:



It is obvious that the presence of impurities in the initial jewelry gold and, consequentially, in the used acid affects the direction of the chemical reaction between aurichlorohydric acid and tetra-*para*-tolylantimony chloride.

According to the X-ray analysis data, the crystal of complex 1 consists of tetra-*para*-tolylstibonium tetrahedral cations and $[p\text{-TolAuCl}_3]^-$ square-planar anions (Fig. 1).

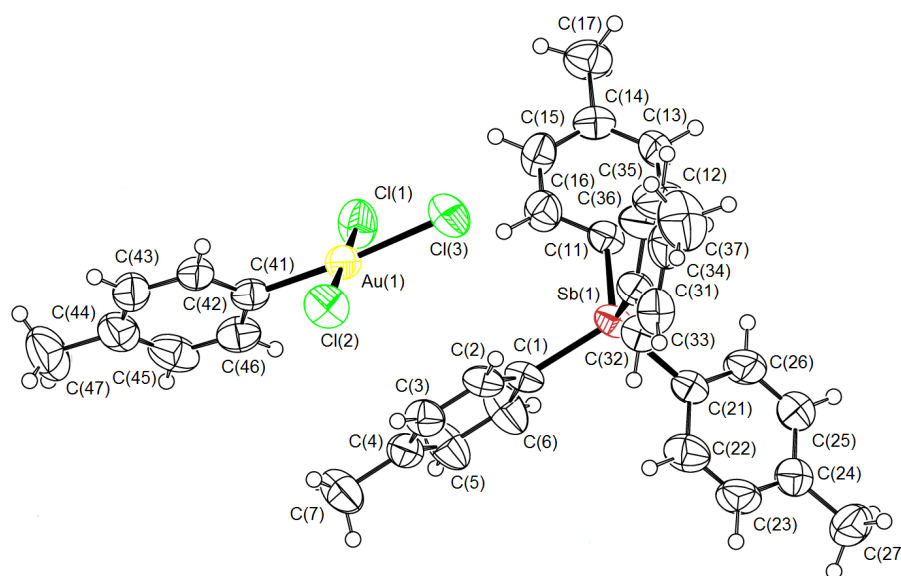


Fig. 1. The structure of the molecule of compound 1

In crystal **1** tetra-*para*-tolylstibonium tetrahedral cations (Sb–C 2.091(7)–2.097(6) Å, CSbC 106.1(3)°–112.7(3)°) are present, as well as [*p*-TolAuCl₃][–] anions of square-planar structure (Au–Cl 2.286(2)–2.389(2) Å, Au–C 2.028(7) Å, ClAuCl 89.92(9)°, 92.42(9)°, 176.68(8)°, CAuCl 88.27(18)°, 89.57(18)°, 175.59(19)°). In crystal **2** the geometric characteristics of cations (Sb–C 2.076(7)–2.097(9), CSbC 106.5(3)°–111.5(4)°) and [AuCl₄][–] square-planar anions (Au–Cl 2.248(3)–2.278(3) Å, ClAuCl 89.17(9)°–90.74(13)°, 177.24(16)°, 177.61(13)°) (Fig. 2, Table 2) are similar to those found in **1**.

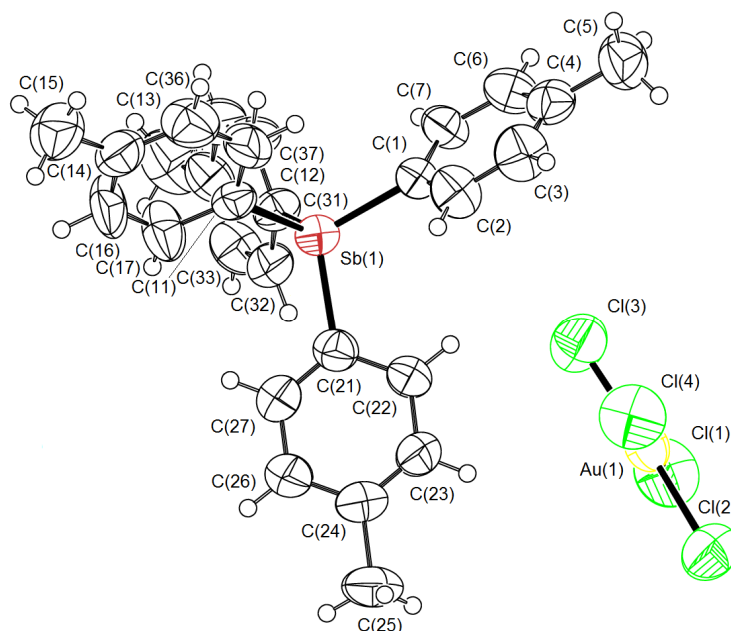


Fig. 2. The structure of complex **2**

The structural organization in crystals I and II is caused by weak interionic hydrogen bonds. At that in I the single interionic contact is observed: *ortho*-H_{Ph}(16)⋯Cl(1) (2.92 Å). In complex II each anion is bonded with four cations through Cl⋯H bonds, formed with the use of all four chlorine atoms and *ortho*-, *meta*- and methyl hydrogen atoms of tolyl substituents (2.81–2.88 Å) (Fig. 3).

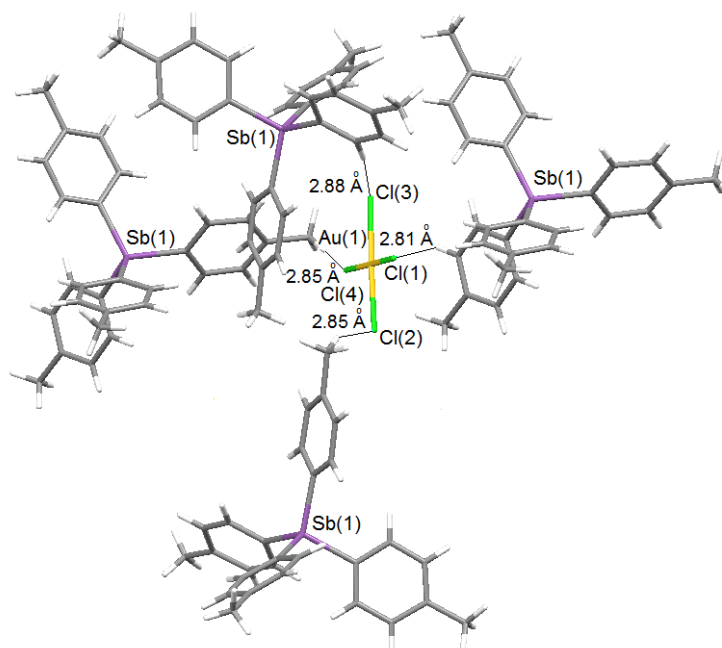


Fig. 3. Interionic hydrogen bonds in the crystal of complex **2**

Conclusions

Thus, the ionic complexes of gold with tetra-*para*-stibonium tetrahedral cation and $[p\text{-TolAuCl}_3]^-$ and $[\text{AuCl}_4]^-$ square-planar anions have been synthesized and structurally described for the first time. The first example of transmetalation reaction with the use of antimony and gold compounds has been described.

References

1. Sharutin V.V., Senchurin V.S., Fastovets O.A., Pakurina A.P., Sharutina O.K. [Synthesis and Structure of Mixed-ligand Complex Compounds of Antimony $[\text{Et}_2\text{NH}_2]_4^+ [\text{SbCl}_2\text{Hal}_4]^{3-} [\text{Cl}]^{1-}$ (Hal = I, Br) and Gold $[\text{Ph}_3\text{PMe}]_2^+ [\text{AuCl}_2\text{Br}_2]^{1-} [\text{AuHal}_2]^{1-}$ (Hal = Cl, Br)]. *Russian Journal Butlerov Communication*, 2007, vol. 11, no. 2, pp. 43–48. (in Russ.)
2. Sharutin V.V., Senchurin V.S., Fastovets O.A., Pakurina A.P., Sharutina O.K. [Tetrafenylantimony(V) Gexachloroplatinate, Tetrachloroaurate, and Gexachlorostannate $[\text{Ph}_4\text{Sb}]_2^+ [\text{PtCl}_6]^{2-}$, $[\text{Ph}_4\text{Sb}]^+ [\text{AuCl}_4]^-$, $[\text{Ph}_4\text{Sb}]_2^+ [\text{SnCl}_6]^{2-}$: Synthesis and Crystal Structures]. *Russian Journal of Coordination Chemistry*, 2008, vol. 34, no. 5, pp. 367–373. DOI: 10.1134/S1070328408050096
3. Sharutin V.V., Senchurin V.S., Sharutina O.K., Vinokurova L.N. [Synthesis and Crystal Structure of Tetrachloroaurate butyltrifenyolphosphonium $[\text{Ph}_3\text{BuP}]^+ [\text{AuCl}_4]^-$]. *Russian Journal Butlerov Communication*, 2011, vol. 27, no. 16, pp. 68–71. (in Russ.)
4. Sharutin V.V., Sharutina O.K., Senchurin V.S. [Synthesis and Crystal structure of acetyltriphénylphosphonium tetrachloroaurate $[\text{Ph}_3\text{PCH}_2\text{C}(\text{O})\text{CH}_3]^+ [\text{AuCl}_4]^-$]. *Russian Journal Butlerov Communication*, 2014, vol. 38, no. 5, pp. 151–154. (in Russ.)
5. Cambridge Crystallographic Data Center. 2015 (deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).
6. SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., 1998, Madison, Wisconsin, USA.
7. SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., 1998, Madison, Wisconsin, USA.
8. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.*, 2009, vol. 42, pp. 339–341. DOI:10.1107/S0021889808042726.

Received 10 September 2015

УДК 541.49+546.593+546.865+547.53.024+548.312.2

DOI: 10.14529/chem150413

СИНТЕЗ И СТРУКТУРА КОМПЛЕКСОВ ЗОЛОТА [*p*-Tol₄Sb][*p*-TolAuCl₃] AND [*p*-Tol₄Sb][AuCl₄]

В.В. Шарутин, О.К. Шарутина, В.С. Сенчурин
Южно-Уральский государственный университет, г. Челябинск

Взаимодействием хлорида тетра-*пара*-толилстибония с тетрагидратом золотохлористоводородной кислоты в ацетоне синтезированы комплексы золота $[\text{p-Tol}_4\text{Sb}]^+[\text{p-TolAuCl}_3]^-$ (**1**) и $[\text{p-Tol}_4\text{Sb}]^+[\text{AuCl}_4]^-$ (**2**). В **1** катионы тетра-*пара*-толилстибония тетраэдрические (Sb-C 2.091(7)-2.097(6) Å, CSbC 106.1(3)^o-112.7(3)^o), анионы $[\text{p-TolAuCl}_3]^-$ имеют плоскочувратное строение (Au-Cl 2.286(2)-2.389(2) Å, Au-C 2.028(7) Å, ClAuCl 89.92(9)^o, 92.42(9)^o, 176.68(8)^o, SAuCl 88.27(18)^o, 89.57(18)^o, 175.59(19)^o). В кристалле **2** геометрические характеристики катионов (Sb-C 2.076(7)-2.097(9), CSbC 106.5(3)^o-111.5(4)^o) и плоскочувратных анионов $[\text{AuCl}_4]^-$ (Au-Cl 2.248(3)-2.278(3) Å, ClAuCl 89.17(9)^o-90.74(13)^o, 177.24(16)^o, 177.61(13)^o) близки к найденным в **1**.

Ключевые слова: синтез, строение, соединения золота, строение, рентгеноструктурный анализ.

Литература

1. Синтез и строение смешаннолигандных комплексных соединений сурьмы [Et₂NH₂]₄⁺[SbCl₂Hal₄]³⁻[Cl]¹⁻ (Hal = I, Br) и золота [Ph₃PMe]₂⁺[AuCl₂Br₂]¹⁻[AuHal₂]¹⁻ (Hal = Cl, Br) / В.В. Шарутин, В.С. Сенчурин, О.А. Фастовец и др. // Бутлеровские сообщения. – 2007. – Т. 11, № 2. – С. 43–48.
2. Синтез и кристаллические структуры гексахлороплатината, тетрахлоороурата и гексахлороостанната тетрафенилсурьмы (V) [Ph₄Sb]₂⁺[PtCl₆]²⁻, [Ph₄Sb]⁺[AuCl₄]⁻, [Ph₄Sb]₂⁺[SnCl₆]²⁻ / В.В. Шарутин, В.С. Сенчурин, О.А. Фастовец и др. // Коорд. химия. – 2008. – Т. 34, № 5. – С. 373–379.
3. Синтез и кристаллическая структура тетрахлоороурата бутилтрифенилфосфония [Ph₃BuP]⁺[AuCl₄]⁻ / В.В. Шарутин, В.С. Сенчурин, О.К. Шарутина, Л.Н. Винокурова // Бутлеровские сообщения. – 2011. – Т. 27, № 16. – С. 68–71.
4. Шарутин, В.В. Синтез и кристаллическая структура тетрахлоороурата ацетонилтрифенилфосфония [Ph₃PCH₂C(O)CH₃]⁺[AuCl₄]⁻ / В.В. Шарутин, О.К. Шарутина, В.С. Сенчурин // Бутлеровские сообщения. – 2014. – Т. 38, № 5. – С. 151–154.
5. Cambridge Crystallographic Data Center. – 2015. – <http://deposit@ccdc.cam.ac.uk> / <http://www.ccdc.cam.ac.uk>.
6. SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. – Madison (Wisconsin, USA): Bruker AXS Inc., 1998.
7. SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. – Madison (Wisconsin, USA): Bruker AXS Inc., 1998.
8. OLEX2: a complete structure solution, refinement and analysis program / O.V. Dolomanov, L.J. Bourhis, R.J. Gildea et al. // J. Appl. Cryst. – 2009. – V. 42. – P. 339–341.

Шарутин Владимир Викторович – доктор химических наук, профессор, старший научный сотрудник УНИД, Южно-Уральский государственный университет. 454080, г. Челябинск, пр. им. В.И. Ленина, 76. E-mail: vvsharutin@rambler.ru

Шарутина Ольга Константиновна – доктор химических наук, профессор, кафедра аналитической химии, Южно-Уральский государственный университет. 454080, г. Челябинск, пр. им. В.И. Ленина, 76. E-mail: sharutinao@mail.ru

Сенчурин Владислав Станиславович – кандидат химических наук, доцент, кафедра органической химии, Южно-Уральский государственный университет. 454080, г. Челябинск, пр. им. В.И. Ленина, 76. E-mail: senvl@rambler.ru

Поступила в редакцию 10 сентября 2015 г.

ОБРАЗЕЦ ЦИТИРОВАНИЯ

Sharutin, V.V. Synthesis and structure of gold complexes [*p*-Tol₄Sb][*p*-TolAuCl₃] and [*p*-Tol₄Sb][AuCl₄] / V.V. Sharutin, O.K. Sharutina, V.S. Senchurin // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 4. – С. 98–103. DOI: 10.14529/chem150413

FOR CITATION

Sharutin V.V., Sharutina O.K., Senchurin V.S. Synthesis and Structure of Gold Complexes [*p*-Tol₄Sb][*p*-TolAuCl₃] and [*p*-Tol₄Sb][AuCl₄]. *Bulletin of the South Ural State University. Ser. Chemistry.* 2015, vol. 7, no. 4, pp. 98–103. DOI: 10.14529/chem150413