ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 2, pp. 124–128. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © V.V. Sharutin, O.K. Sharutina, V.S. Senchurin, A.N. Neudachina, 2016, published in Koordinatsionnaya Khimiya, 2016, Vol. 42, No. 2, pp. 110–115.

Synthesis and Structure of Silver Complexes: $[Ph_3PC_3H_5\text{-}cyclo]_2^+[AgBr_3]^{2-}$, $[Ph_3PC_3H_5\text{-}cyclo]_n^+[Ag_2Br_3]_n^{n-}$

V. V. Sharutin*, O. K. Sharutina, V. S. Senchurin, and A. N. Neudachina

National Research Southern Ural State University, Chelyabinsk, Russia
**e-mail: vvsharutin@rambler.ru*

Received April 22, 2015

Abstract—The reaction of triphenylcyclopropylphosphonium bromide with silver bromide (2 : 1 or 1 : 2 molar ratio) gave the complexes $[Ph_3PC_3H_5\text{-}cyclo]_2^+[AgBr_3]^{2-}$ (**I**) and $[Ph_3PC_3H_5\text{-}cyclo]_n^+[Ag_2Br_3]_n^{n-}$ (**II**). According to X-ray diffraction data (CIF files CCDC no. 1010694 (**I**), 999903 (**II**)), the complexes consist of tetrahedral triphenylcyclopropylphosphonium cations and monomeric $[AgBr_3]^{2-}$ (**I**) or polymeric $[Ag_2Br_3]_n^{n-}$ anions (**II**). The C.N.(Ag^+) in **I** is 3 and that in **II** is 4; The C.N.(Br^-) in the polymeric anion is 4 or 2. The structural organization of the crystals is formed by weak hydrogen bonds.

DOI: 10.1134/S107032841602007X

INTRODUCTION

Quite a number of silver complexes with ammonium cations and mono-, bi-, or polynuclear Ag-, Cl-containing anions have been structurally characterized [1]. Meanwhile, complexes with phosphonium cations and Br-containing anions have been barely studied [2, 3].

This paper presents a study of the reactions of triphenylcyclopropylphosphonium bromide with silver bromide in various molar ratios and determination of the structures of the resulting addition complexes $[Ph_3PC_3H_5\text{-}cyclo]_2^+[AgBr_3]^{2-}$ (**I**) and $[Ph_3PC_3H_5\text{-}cyclo]_n^+ [Ag_2Br_3]_n^{n-}$ (**II**).

EXPERIMENTAL

Synthesis of I. A mixture of triphenylcyclopropylphosphonium bromide (0.208 g, 0.54 mmol) and silver bromide (0.051 g, 0.27 mmol) was dissolved with stirring in 2 mL of dimethyl sulfoxide. After solvent evaporation to a volume of 0.5 mL, colorless crystals were formed. The yield of complex **I** was 0.166 g (64%); T_m 119°C.

For $C_{42}H_{40}P_2Br_3Ag$

anal. calcd., %:	C, 52.85;	H, 4.19.
Found, %:	C, 52.69;	H, 4.28.

IR (ν, cm^{-1}): 3055, 2996, 1632, 1585, 1479, 1435, 1338, 1316, 1292, 1196, 1180, 1113, 1073, 1050, 1024, 996, 939, 897, 867, 833, 798, 753, 719, 692, 661, 531, 499, 458, 438.

Synthesis of II. A mixture of triphenylcyclopropylphosphonium bromide (0.104 g, 0.27 mmol) and silver bromide (0.102 g, 0.54 mmol) was dissolved with stirring in 3 mL of dimethyl sulfoxide. After solvent evaporation to a volume of 0.5 mL, colorless crystals were formed. The yield of complex **II** was 0.148 g (72%); $T_{decomp} = 65°C$.

For $C_{21}H_{20}PBr_3Ag_2$

anal. calcd., %:	C, 33.20;	H, 2.64.
Found, %:	C, 33.07;	H, 2.75.

IR (ν, cm^{-1}): 3052, 2990, 2968, 1667, 1632, 1585, 1483, 1437, 1338, 1314, 1299, 1198, 1113, 1069, 1022, 996, 953, 897, 867, 837, 792, 751, 725, 690, 661, 528, 496, 448.

The IR spectra of compounds **I** and **II** were recorded on a Bruker Tensor 27 IR spectrometer in the 4000–400 cm^{-1} range (KBr pellets).

X-ray diffraction study of the crystals **I** and **II** was carried out on a D8 QUEST Bruker diffractometer (MoK_α radiation, $\alpha = 0.71073$ Å, graphite monochromator). The data were collected and edited, the unit cell parameters were refined, and absorption corrections were applied using SMART and SAINT-Plus software [4]. All calculations for structure solution and refinement were carried out using SHELXL/PC [5] and OLEX2 software [6]. The structures were solved by direct method and refined by the least squares method in the anisotropic approximation for non-hydrogen atoms. The crystal characteristics and refinement details for structures **I** and **II** are summarized in Table 1; selected bond lengths and bond angles are presented in Table 2.

Table 1. Crystal characteristics and X-ray data collection and refinement details for **I** and **II**

Parameter	Value	
	I	**II**
M	477.14	758.81
T, K	296(2)	296(2)
System	Monoclinic	Orthorhombic
Space group	Cc	$P2_12_12_1$
a, Å	10.0134(6)	7.1239(2)
b, Å	23.7364(15)	15.4112(6)
c, Å	17.2157(11)	20.6800(7)
β, deg	101.712(2)	90.00
V, Å^3	4006.7(4)	2270.41(13)
Z	8	4
ρ(calcd.), g/cm^3	1.582	2.220
μ, mm^{-1}	3.603	7.080
F(000)	1896.0	1440.0
Crystal size, mm	0.67 × 0.32 × 0.3	1.01 × 0.38 × 0.36
Range of θ, deg	5.952–52.842	6.04–52.8
Ranges of reflection indices	$-12 \leqslant h \leqslant 11, -29 \leqslant k \leqslant 29, -21 \leqslant l \leqslant 21$	$-8 \leqslant h \leqslant 8, -18 \leqslant k \leqslant 19, -25 \leqslant l \leqslant 25$
Number of measured reflections	40976	21223
Number of unique reflections (R_{int})	8004 (0.0544)	4626 (0.0361)
Reflections with $F^2 > 2\sigma(F^2)$	4012	2406
Number of parameters refined	433	245
GOOF	1.017	1.025
R-factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0431, wR_2 = 0.0976$	$R_1 = 0.0288, wR_2 = 0.0613$
R-factors for all reflections	$R_1 = 0.0692, wR_2 = 0.1077$	$R_1 = 0.0395, wR_2 = 0.0658$
Residual electron density (max/min), e/Å^3	0.65/–0.44	0.65/–0.77

The full tables of atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (no. 1010694 (**I**), 999903 (**II**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

We studied the reaction between silver bromide and triphenylcyclopropylphosphonium bromide in different molar ratios in a dimethyl sulfoxide solution. The reaction at 2 : 1 molar ratio was found to afford addition complex **I** with the $[AgBr_3]^{2-}$ anion:

$$2Ph_3(cyclo\text{-}C_3H_5)PBr + AgBr$$
$$\rightarrow [Ph_3(cyclo\text{-}C_3H_5)P]_2^+[AgBr_3]^{2-}.$$

When the molar ratio is 1 : 2, the reaction gives complex **II** with anion of a different structure:

$$nPh_3(cyclo\text{-}C_3H_5)PBr + 2n\ AgBr$$
$$\rightarrow [\mathrm{Ph3(cyclo\text{-}C3H5)P}]_n^+[\mathrm{Ag2Br3}]_n^{n-}.$$

The structures of complexes **I** and **II** were determined by X-ray diffraction. The crystal of complex **I** consists of two types of crystallographically independent triphenylcyclopropylphosphonium cations and $[AgBr_3]^{2-}$ anions (Fig. 1a).

In the tetrahedral cations, the CPC angles vary in the range of 107.3(2)°–111.3(2)°. The P–C distances (1.766(4)–1.800(5) Å) are somewhat shorter than the sum of the covalent radii of phosphorus and carbon atoms (1.88 Å [7]). In the nearly planar $[AgBr_3]^{2-}$ anion (the silver atom deviates from the $[Br_3]$ plane by 0.076 Å), the BrAgBr angles are 114.31(3)°, 119.66(3)°, and 125.77(4)°, while the Ag–Br bond length varies in the 2.5542(13)–2.6064(9) Å range. Tight H···Ag contacts (2.68 Å) and weak H···Br hydrogen bonds (2.88–2.98 Å) are present in the crystal of **I** (Fig. 2).

The geometric characteristics of the cations (CPC, 107.4(2)°–111.99(19)°; P–C, 1.766(5)–1.800(4) Å) in **II** are similar to those in **I**. The polymeric anion has an unusual design (Fig. 1b). The silver atoms are four-

Table 2. Bond lengths (d) and bond angles (ω) in structures **I** and **II***

Bond	d, Å	Angle	ω, deg
I			
Br(1)–Ag(1)	2.5929(9)	Br(1)Ag(1)Br(3)	114.31(3)
Ag(1)–Br(2)	2.5542(13)	Br(2)Ag(1)Br(1)	119.66(3)
Ag(1)–Br(3)	2.6064(9)	Br(2)Ag(1)Br(3)	125.77(4)
P(1)–C(1)	1.789(4)	C(11)P(1)C(1)	111.1(2)
P(1)–C(41)	1.771(5)	C(21)P(1)C(1)	107.3(2)
P(1)–C(11)	1.785(4)	C(21)P(1)C(11)	109.8(2)
P(1)–C(21)	1.785(5)	C(71)P(2)C(61)	109.7(2)
P(2)–C(61)	1.798(4)	C(71)P(2)C(51)	108.5(2)
P(2)–C(71)	1.793(4)	C(81)P(2)C(61)	107.4(2)
P(2)–C(81)	1.766(4)	C(81)P(2)C(71)	110.6(2)
P(2)–C(51)	1.800(5)	C(81)P(2)C(51)	111.3(2)
II			
Ag(1)–Br(1)	2.6292(7)	Br(1)Ag(1)Br(2a)	118.12(2)
Ag(1)–Br(2)	2.8355(7)	Br(1)Ag(1)Br(2)	99.03(2)
Ag(1)–Br(2a)	2.8964(7)	Br(1)Ag(1)Br(3)	130.17(3)
Ag(1)–Br(3)	2.6364(7)	Br(2)Ag(1)Br(2a)	99.916(19)
Br(1)–Ag(2)	2.6644(7)	Br(3)Ag(1)Br(2)	112.01(2)
Ag(2)–Br(2b)	2.7855(7)	Br(3)Ag(1)Br(2a)	94.43(2)
Ag(2)–Br(2)	2.8052(7)	Ag(1)Br(1)Ag(2)	82.888(19)
Ag(2)–Br(3d)	2.6799(7)	Br(1)Ag(2)Br(2b)	116.48(2)
P(1)–C(21)	1.792(4)	Br(1)Ag(2)Br(2)	98.95(2)
P(1)–C(1)	1.784(4)	Br(1)Ag(2)Br(3c)	125.71(3)
P(1)–C(7)	1.766(5)	Br(2b)Ag(2)Br(2)	103.427(18)
P(1)–C(11)	1.800(4)	Br(3c)Ag(2)Br(2)	115.01(2)
Br(2)–Ag(1b)	2.8964(7)	Br(3c)Ag(2)Br(2b)	96.07(2)
Br(2)–Ag(2a)	2.7855(7)	Ag(1)Br(2)Ag(1b)	126.794(17)
Br(3)–Ag(2d)	2.6800(7)	Ag(2a)Br(2)Ag(1)	78.98(2)
C(1)–C(6)	1.380(6)	Ag(2)Br(2)Ag(1)	76.803(16)
C(1)–C(2)	1.383(6)	Ag(2a)Br(2)Ag(1b)	79.225(17)
C(6)–C(5)	1.397(6)	Ag(2)Br(2)Ag(1b)	77.638(19)
C(5)–C(4)	1.354(6)	Ag(2a)Br(2)Ag(2)	125.423(18)
C(4)–C(3)	1.363(7)	Ag(1)Br(3)Ag(2d)	85.936(18)
C(7)–C(9)	1.495(6)	C(21)P(1)C(11)	109.2(2)
C(7)–C(8)	1.493(6)	C(1)P(1)C(21)	111.99(19)
C(9)–C(8)	1.456(8)	C(1)P(1)C(11)	107.4(2)
C(11)–C(12)	1.383(6)	C(7)P(1)C(21)	108.7(2)
C(11)–C(16)	1.386(6)	C(7)P(1)C(1)	110.6(2)
C(12)–C(13)	1.388(6)	C(7)P(1)C11	109.0(2)

* Symmetry codes: (a) $1/2 + x, -5/2 - y, -z$; (b) $-1/2 + x, -5/2 - y, -z$; (c) $-1 + x, y, z$; (d) $1 + x, y, z$.

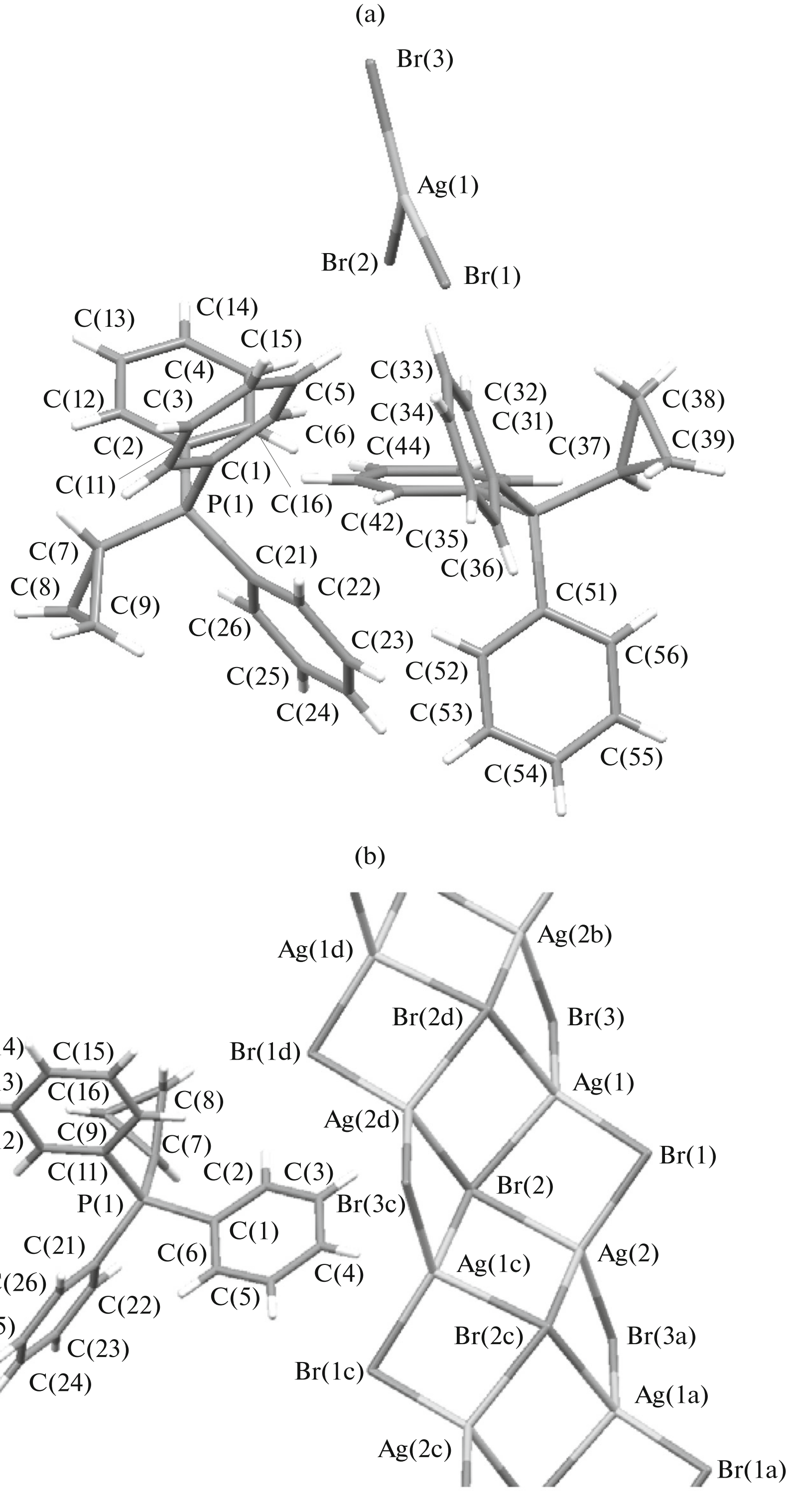

Fig. 1. Structure of complexes (a) **I** and (b) **II**.

coordinate. The BrAg(1)Br and BrAg(2)Br angles vary in the ranges of 94.43(2)°–130.17(3)° and 96.07(2)°–127.71(3)°, which is indicative of pronounced distortion. The Ag(1)–Br(1,2,2a,3) distances are 2.6292(7), 2.8355(7), 2.8964(7), and 2.6367(7) Å, and the Ag(2)–Br(1,2,2b,3d) distances are 2.6644(7), 2.8052(7), 2.7855(7), and 2.6799(7) Å.

The bromine atoms are in contact with four (two) neighboring atoms (the AgBr(2)Ag angles are

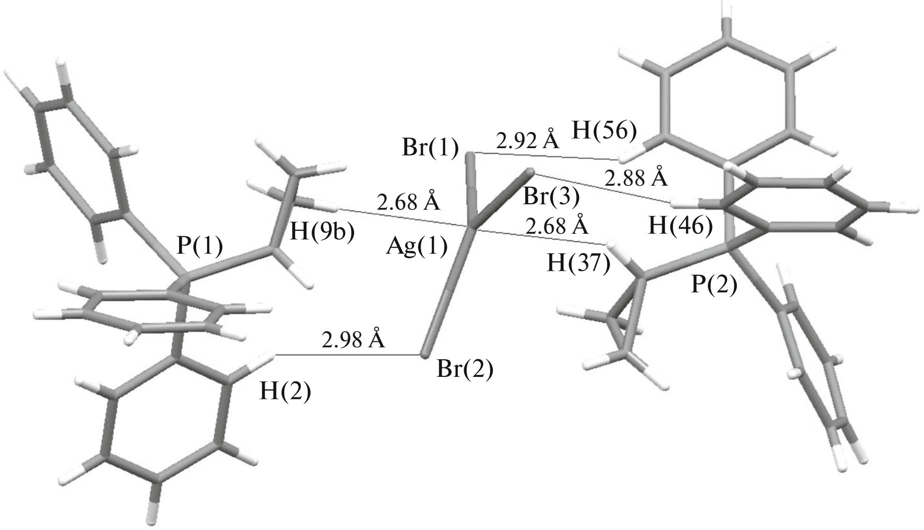

Fig. 2. Ion–ion contacts in the crystal of complex **I**.

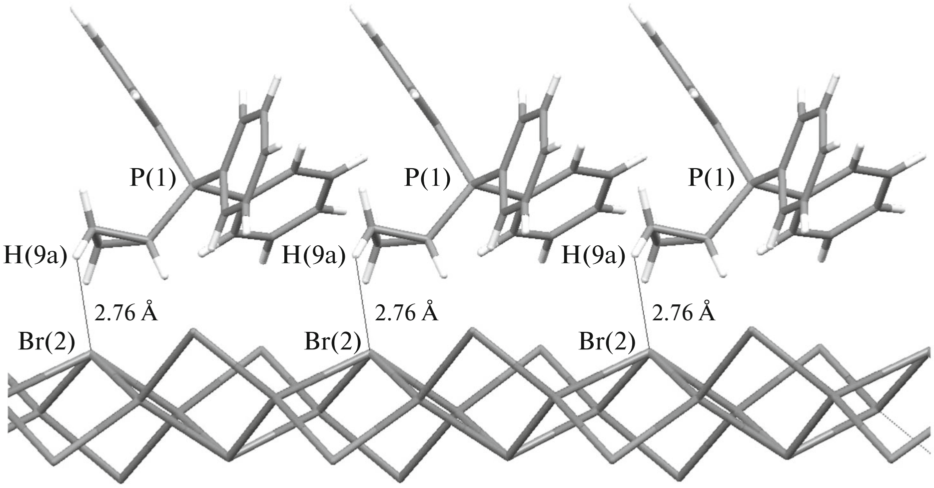

Fig. 3. Hydrogen bonds in the crystal of complex **II**.

76.80(2)°, 77.64(2)°, 78.98(2)°, and 79.23(2)°, while the Ag(1)Br(1)Ag(2) and Ag(1)Br(3)Ag(2b) angles are 82.89(2)° and 85.94(2)°, respectively. As was to be expected, the Ag–Br(1,3) distances are shorter than Ag–Br(2).

The structural organization of complex **II** is formed by H···Br hydrogen bonds (2.76 Å) (Fig. 3).

REFERENCES

1. *Cambridge Crystallografic Database. Release 2015.*
2. Sharutin, V.V., Sharutina, O.K., Senchurin, V.S., and Neudachina, A.N., *Butlerovskie Soobshcheniya*, 2014, vol. 39, no. 10, p. 54.
3. Helgesson, G. and Jagner, S., *J. Chem. Soc., Dalton Trans.(1972–1999)*, 1988, p. 2117.
4. *SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System*, Madison: Bruker AXS Inc., 1998.
5. *SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, Madison: Bruker AXS Inc., 1998.
6. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339.
7. Batsanov, S.S., *Zh. Neorg. Khim.*, 1991, vol. 36, no. 12, p. 3015.

Translated by Z. Svitanko