ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2008, Vol. 34, No. 3, pp. 175–178. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.V. Sharutin, A.P. Pakusina, I.V. Egorova, O.K. Sharutina, M.A. Pushilin, 2008, published in Koordinatsionnaya Khimiya, 2008, Vol. 34, No. 3, pp. 181–184.

New Crystalline Modification of μ-Oxo-bis(bromotriphenylantimony)

V. V. Sharutin[a], **A. P. Pakusina**[a], **I. V. Egorova**[a], **O. K. Sharutina**[a], **and M. A. Pushilin**[b]

[a] *Blagoveshchensk State Pedagogical University, Blagoveshchensk, Russia*

[b] *Institute of Chemistry, Far East Division, Russian Academy of Sciences,*
pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia

E-mail: vvsharutin@rambler.ru

Received February 14, 2007

Abstract—The triclinic crystalline modification of μ-oxo-bis(bromotriphenylantimony) has been synthesized by the reaction of triphenylantimmony dibromide with water in benzene. The Sb atoms have distorted trigonal bipyramidal coordination with the bromine atoms and bridging oxygen atoms in the axial positions. The distances are Sb–C 2.104(2)–2.123(2), Sb(1)–Br(1) 2.7492(2), Sb(2)–Br(2) 2.7235(2), Sb(1)–O 1.986(1), and Sb(2)–O 1.987(1) Å, and the Sb(1)OSb(2) angle is 138.19(6)°.

DOI: 10.1134/S1070328408030044

INTRODUCTION

It is known that the crystallization conditions sometimes influence the type of the crystal lattice and geometric parameters of the molecules in a crystal. For instance, the recrystallization of μ-oxo-bis(iodotriphenylantimony) from acetonitrile affords yellow crystals containing molecules with the bent SbOSb fragment, while in dichloromethane, colorless crystals with the linear SbOSb group are formed [1].

In this paper, we report the synthesis of structural isomers of μ-oxo-bis(bromotriphenylstibium) (**I**, **II**) and the results of X-ray diffraction analysis of triclinic modification **II**.

EXPERIMENTAL

Synthesis of the monoclinic modification of μ-oxo-bis(bromotriphenylantimony) (I). Water (1 ml) was added to a solution of triphenylantimony dibromide (1.03 g, 1.0 mmol) in acetone (50 ml), and the mixture was refluxed for 1 h. After acetone evaporated, colorless crystals of compound **I** were obtained as rectangular plates with mp 247°C (mp 247°C) [2, 3]. The yield was 0.73 g (83%).

Synthesis of triclinic modification II. A mixture of triphenylantimony dibromide (1.03 g, 1.0 mmol) and water (1 ml) in benzene (100 ml) was refluxed for 1 h. Heptane (10 ml) was added to the cooled solution, and the solvent was evaporated slowly. Large pale yellow crystals of isomer **II** with mp 247°C were obtained. The yield was 0.60 g (68%).

The IR spectrum of isomer **II** was recorded on a Shimadzu spectrometer in Nujol (KBr plates). IR (ν, cm^{-1}): 418.55, 451.34, 688.59, 736.81, 777.31, 848.68, 896.90, 937.40, 970.19, 997.20, 1020.34, 1066.64, 1089.78, 1157.29, 1180.44, 1271.09, 1305.81, 1330.88, 1435.04, 1573.91, 2852.72, 2922.16, 2951.09.

X-ray diffraction study of crystals **II** was carried out on a SMART-1000 CCD diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator).

The structure was solved by the direct method and refined by the least-squares calculation in the anisotropic approximation for non-hydrogen atoms. The positions of the hydrogen atoms were calculated geometrically and included into the refinement in the riding model.

The data were collected and edited and the unit cell parameters were refined using the SMART and SAINT-*Plus* programs [4]. All calculations for the structure determination and refinement were performed using the SHELXTL/PC program packages [5].

The main crystallographic data and results of refinement of structure **II** are listed in Table 1, coordinates and temperature factors of atoms are summarized in Table 2, and bond lengths and bond angles are presented in Table 3.

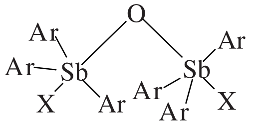
RESULTS AND DISCUSSION

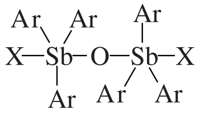
The geometries of the molecules of compounds $(Ar_3SbX)_2O$ with trigonal bipyramidal coordination of

Table 1. Crystallographic data and experimental and refinement details for structure **II**

Parameter	Value
Empirical formula	$C_{36}H_{30}Br_2OSb_2$
FW	881.92
T, K	203(1)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell parameters:	
a, Å	9.4599(3)
b, Å	11.1069(4)
c, Å	16.0196(5)
α, deg	82.684(1)
β, deg	84.320(1)
γ, deg	74.394(1)
V, Å^3	1604.2(1)
Z	2
ρcalcd, g/cm^3	1.826
μ_{Mo}, mm^{-1}	4.202
$F(000)$	852
Crystal shape (size, mm)	0.20 × 0.20 × 0.10
θ range, deg	2.68–31.51
Index range	$-13 \le h \le 12$, $-16 \le k \le 13$, $-16 \le l \le 23$
Total number of reflections	13644
Number of unique reflections	10032 ($R_{int} = 0.0645$)
Number of reflections with $I > 2\sigma(I)$	8176
Number of refined parameters	370
GOOF	1.036
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0332$, $wR_2 = 0.0828$
R factors for all reflections	$R_1 = 0.0449$, $wR_2 = 0.0885$
Residual electron density (min/max), e/Å^3	–1.315/0.853

the antimony atoms mainly differ in the structure of the SbOSb fragment. In most cases, the bent SbOSb fragment is observed, while molecules with the linear arrangement of atoms are rarely encountered [1–3, 6].





Although the structures of many compounds of the type considered have been determined by the present time, the question about the factors affecting the value of the angle at the bridging oxygen atom remains open. We attempted to determine the influence of the synthesis conditions of μ-oxo-bis(bromotriphenylantimony) on the crystal geometry of the molecules.

The colorless crystals of compound **I** (mp 247°C) prepared by hydrolysis of Ph_3SbBr_2 (acetone, 20°C, 1 h) are monoclinic [2, 3]:

$$2Ph_3SbBr_2 + H_2O \longrightarrow (Ph_3SbBr)_2O + 2HBr.$$

The crystal of compound **I** contains two types of crystallographically independent and almost linear molecules (SbOSb 168.4° and 174.7° [2]; 170.05° and 175.65° [3]).

When the reaction is carried out in benzene, large pale yellow trigonal prisms (mp 247°C)) of triclinic crystalline modification **II** were isolated from the reaction mixture.

The structural units of crystal **II** are μ-oxo-bis(bromotriphenylantimony) molecules in which two $(C_6H_5)_3SbBr$ fragments are joined by the bridging oxygen atom (figure). The Sb(1) and Sb(2) atoms have slightly distorted trigonal bipyramidal coordination. The CSb(1,2)C equatorial angles lie in the intervals 115.97(7)°–124.32(6)° and 117.53(8)°–124.13(7)°, and the BrSb(1,2)O angles are 175.30(3)° and 178.45(3)°, respectively. The Sb(1)–O, Sb(2)–O, and Sb(1)–Br(1), Sb(2)–Br(2) distances in compound **II** (1.986(1), 1.987(1) and 2.7492(2), 2.7235(2) Å) are somewhat longer than the analogous Sb–O (1.930–1.958 Å) and Sb–Br (2.692–2.722 Å) distances in complex **I** [3]. The Sb–C(Ph) bond lengths in compound **II** (2.104(2)–2.123(2) Å) are typical of organic antimony(V) derivatives. The SbOSb angle in compound **II** (138.19°) is much smaller than similar angles in compound **I** [2, 3].

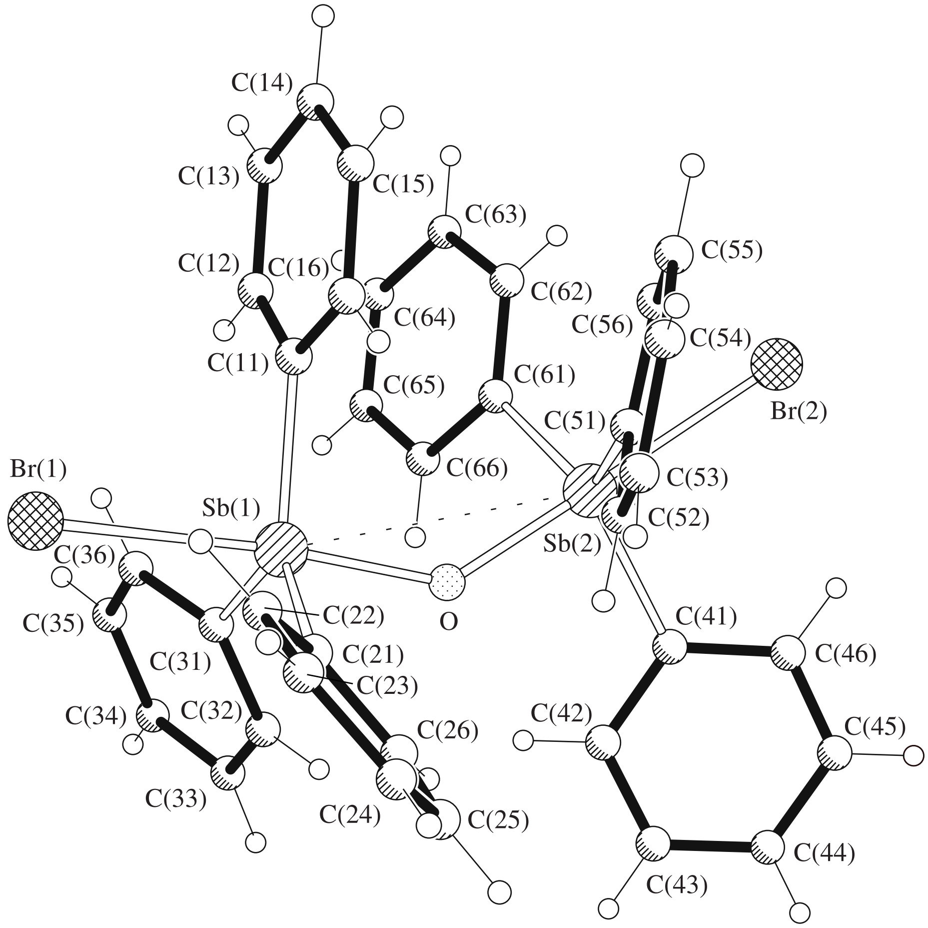
In the bridged antimony compounds, the bent shape of molecules suggests that its peripheral fragments draw together, possibly, due to the π-interaction of the phenyl group at one Sb atom with the second Sb atom,

Table 2. Coordinates of atoms (×10^4) and their isotropic equivalent temperature parameters (×10^3) in structure **II**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Sb(1)	8153.7(1)	613.9(1)	2730.19(6)	21.16(2)
Sb(2)	5299.3(1)	3611.1(1)	2315.60(6)	21.66(2)
Br(1)	10554.5(2)	–1410.7(2)	2576.3(1)	36.38(5)
Br(2)	3818.0(2)	5754.8(2)	1421.6(1)	39.23(5)
O	6423(1)	2042(1)	2943(1)	24.0(3)
C(11)	8646(2)	1163(2)	1452(1)	24.7(4)
C(12)	9726(2)	1797(2)	1234(1)	40.2(5)
C(13)	10044(2)	2168(2)	390(1)	47.7(6)
C(14)	9269(2)	1924(2)	–226(1)	43.2(6)
C(15)	8210(3)	1299(2)	–7(1)	44.1(5)
C(16)	7875(2)	928(2)	835(1)	35.9(4)
C(21)	6801(2)	–652(2)	2970(1)	27.6(4)
C(22)	7017(2)	–1644(2)	2482(1)	38.6(5)
C(23)	5980(2)	–2336(2)	2547(2)	47.4(6)
C(24)	4751(2)	–2054(2)	3101(2)	51.2(6)
C(25)	4556(2)	–1096(2)	3604(2)	46.9(6)
C(26)	5578(2)	–373(2)	3536(1)	36.8(5)
C(31)	9274(2)	1102(1)	3658(1)	24.7(3)
C(32)	8507(2)	1374(2)	4428(1)	28.9(4)
C(33)	9183(2)	1737(2)	5046(1)	37.0(5)
C(34)	10588(2)	1873(2)	4890(1)	39.5(5)
C(35)	11347(2)	1631(2)	4120(1)	40.8(5)
C(36)	10710(2)	1203(2)	3507(1)	34.3(4)
C(41)	3978(2)	4137(2)	3428(1)	28.7(4)
C(42)	4456(3)	3554(2)	4194(1)	60.8(8)
C(43)	3592(4)	3867(3)	4933(2)	79.6(10)
C(44)	2281(3)	4753(2)	4900(2)	60.8(7)
C(45)	1800(2)	5325(2)	4138(2)	48.3(6)
C(46)	2639(2)	5029(2)	3403(1)	37.6(5)
C(51)	4515(2)	2618(2)	1501(1)	27.1(4)
C(52)	4026(2)	1589(2)	1863(1)	30.8(4)
C(53)	3602(2)	849(2)	1345(1)	42.1(5)
C(54)	3703(2)	1139(2)	478(1)	46.3(5)
C(55)	4176(2)	2168(2)	123(1)	46.6(6)
C(56)	4579(2)	2924(2)	637(1)	37.9(5)
C(61)	7192(2)	4295(2)	2029(1)	33.0(4)
C(62)	7544(2)	4817(2)	1234(2)	45.2(6)
C(63)	8815(3)	5234(2)	1106(2)	67.8(8)
C(64)	9696(3)	5153(2)	1747(2)	77.1(10)
C(65)	9342(2)	4627(2)	2544(2)	69.7(8)
C(66)	8091(2)	4184(2)	2687(2)	43.1(5)

Table 3. Selected bond lengths and bond angles in structure **III**

Bond	*d*, Å	Angle	ω, deg
Sb(1)–O	1.986(1)	OSb(1)C(11)	98.30(5)
Sb(1)–C(11)	2.104(2)	OSb(1)C(31)	90.51(5)
Sb(1)–C(31)	2.110(2)	C(11)Sb(1)C(31)	118.94(7)
Sb(1)–C(21)	2.120(2)	OSb(1)C(21)	90.27(5)
Sb(1)–Br(1)	2.7492(2)	C(11)Sb(1)C(21)	115.97(7)
Sb(1)–Sb(2)	3.7108(2)	C(31)Sb(1)C(21)	124.32(6)
Sb(2)–O	1.987(1)	OSb(1)Br(1)	175.30(3)
Sb(2)–C(51)	2.113(2)	C(11)Sb(1)Br(1)	86.26(4)
Sb(2)–C(61)	2.115(2)	C(31)Sb(1)Br(1)	86.26(4)
Sb(2)–C(41)	2.123(2)	C(21)Sb(1)Br(1)	88.74(4)
Sb(2)–Br(2)	2.7235(2)	OSb(2)C(51)	92.83(5)
C(11)–C(16)	1.374(3)	OSb(2)C(61)	92.41(6)
C(11)–C(12)	1.384(3)	C(51)Sb(2)C(61)	124.13(7)
C(12)–C(13)	1.391(3)	OSb(2)C(41)	90.82(5)
C(13)–C(14)	1.379(3)	C(51)Sb(2)C(41)	117.96(7)
C(14)–C(15)	1.361(3)	C(61)Sb(2)C(41)	117.53(8)
C(15)–C(16)	1.390(3)	OSb(2)Br(2)	178.45(3)
C(21)–C(26)	1.389(2)	C(51)Sb(2)Br(2)	86.87(4)
C(21)–C(22)	1.391(3)	C(61)Sb(2)Br(2)	86.51(5)
C(22)–C(23)	1.389(3)	C(41)Sb(2)Br(2)	90.66(4)
C(23)–C(24)	1.382(3)	Sb(1)OSb(2)	138.19(6)



Structure of a molecule of complex **II**.

which is also coordinatively unsaturated (by analogy with the additional coordination in [7]).

REFERENCES

1. Taylor, M.J., Baker, L.-J., Rickard, C.E.F., and Surman, P.W.J., *J. Organomet. Chem.*, 1995, vol. 498, no. 1, p. C14.
2. Sharutin, V.V., Pakusina, A.P., Sharutina, O.K., et al., *Khimiya i Khimicheskoe Modelirovanie. Butlerovskie Soobshcheniya* (Chemistry and Chemical Modeling. Butlerov Communications), 2002, no. 11, p. 13.
3. Ouchi, A. and Sato, S., *Bull. Chem. Soc. Jpn.*, 1988. vol. 61, no. 5, p. 1806.
4. *SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System*, Bruker AXS Inc., Madison (WI, USA), 1998.
5. *SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data*, Bruker AXS Inc., Madison (WI, USA), 1998.
6. Sharutin, V.V., Egorova, I.V., Pavlushkina, I.I., et al., *Koord. Khim.*, 2003, vol. 29, no. 2, p. 89 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 29, no. 2, p. 83].
7. Zakharov, L.N., Sharutin, V.V., Osanova, N.A., et al., *Khimiya Elementoorgan. Soedinenii. Mezhvuz. Sbornik* (Chemistry of Organoelement Compounds. An Inter-University Collection), Gor'Kovskii Gos. Univ., 1984, p. 59.