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Bismuth Compounds $[Ph_3BuP]^+I^-$, $[Ph_3BuP]_2^+[Bi_2I_8 \cdot 2Me_2C{=}O]^{2-}$, and $[Ph_3BuP]_2^+[Bi_2I_8 \cdot 2Me_2S{=}O]^{2-}$: Syntheses and Crystal Structures

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Abstract—The complexes $[Ph_3BuP]]_2^+[Bi_2I_8 \cdot 2Me_2C{=}O]^{2-}$ (**II**) and $[Ph_3BuP]_2^+[Bi_2I_8 \cdot 2Me_2S{=}O]^{2-}$ (**III**) are synthesized by the reactions of triphenyl(*n*-butyl)phosphonium iodide (**I**) with bismuth iodide in acetone and dimethyl sulfoxide. In the cations of complexes **I**–**III**, the P atoms have a distorted tetrahedral coordination (CPC angles 106.3(2)°–112.0(3)°). The butyl group in cation **I** is disordered over two positions. In the binuclear centrosymmetric anions of structures **II** and **III**, the octahedrally coordinated bismuth atoms are linked in pairs by two bridging (br) iodine atoms (Bi–I_{br} 3.1508(7) and 3.2824(8) Å in compound **II**, 3.1961(3) and 3.3108(3) Å in complex **III**), which are coplanar to four terminal (t) iodine atoms (Bi–I_t 2.9260(7) and 2.9953(6) Å in complex **II**, 2.9206(3) and 2.9786(3) Å in complex **III**). The two remaining positions at the bismuth atom are occupied by the iodine atom (Bi–I_t 2.8531(7) Å in complex **II**, 2.8984(3) Å in complex **III**) and O atom of the organic molecule (Bi–O 2.747(6) Å in complex **II**, 2.507(3) Å in complex **III**).

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INTRODUCTION

In terms of the systematic studies of the chemistry and structure of the Bi(III) halide complexes aimed at preparing new substances and materials with valuable properties, we synthesized a large group of iodobismuthates(III) with various organoelement cations. The crystal structures of tetraphenylphosphonium pentaiodo(dimethylsulfoxido)bismuthate and mixed bromine- and iodine-containing Bi(III) complexes were described [1, 2]. The works in this direction are continued by the studies of the reactions of bismuth iodide with triphenyl(*n*-butyl)phosphonium iodide and the influence of the solvent nature on the structures of the anions of the formed complexes.

EXPERIMENTAL

Synthesis of $[Ph_3BuP]_2^+[Bi_2I_8 \cdot 2Me_2C{=}O]^{2-}$ (II). A mixture of triphenyl(*n*-butyl)phosphonium iodide (**I**) (0.89 g), bismuth iodide (1.18 g), and acetone (50 ml) was stirred at 20°C for 1 h. A red-orange solution was evaporated to a volume of 1 ml, and the red-orange crystals that formed were filtered and dried. The yield of complex **II** was 2.08 (95%)), mp = 74°C.

IR (cm^{-1}): 503 w, 529 m, 690 s, 729 s, 994 w, 1110 s, 1440 s, 1634 s, 2895 w, 2919 m, 2952 w.

For $C_{50}H_{60}O_2Bi_2I_8P_2$ anal. calcd. (%): C, 27.74; H, 2.74.

Found (%): C, 27.30; H, 2.57.

Synthesis of $[Ph_3BuP]_2^+[Bi_2I_8 \cdot 2Me_2S{=}O]^{2-}$ (III). A mixture of bismuth iodide (1.18 g), compound **I** (0.89 g), and dimethyl sulfoxide (25 ml) were stirred at 20°C for 1 h. An orange solution was evaporated to a volume of 1 ml, and the orange crystals that formed were filtered and dried. The yield of complex **III** was 1.41 g (98%), mp = 188°C.

IR (cm^{-1}): 497 m, 535 m, 690 m, 734 m, 840 w, 936 s, 987 m, 1026 s, 1110 s, 1188 w, 1336 w, 1440 m, 2861 w, 2919 m, 2964 w.

For $C_{48}H_{60}O_2Bi_2I_8P_2S_2$ anal. calcd. (%): C, 25.85; H, 2.69.

Found (%): C, 25.38; H, 2.71.

The IR spectra of complexes **II** and **III** were recorded on a 1201 FT-IR spectrometer (KBr pellets).

X-ray diffraction analyses of crystals **I** and **II** were carried out on a Bruker P4 diffractometer and that for complex **III** was carried out on a SMART-1000 CCD diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator).

The data were collected and edited, the unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-*Plus* program packages [3]. All calculations on structure determination and refinement were performed by the SHELXL/PC program package [4]. Structures **I**–**III** were determined by a direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms.

Table 1. Crystallographic data and experimental and refinement details for structures **I–III**

Parameter	Value		
	I	II	III
FW	446.28	2188.08	2228.18
T, K	296(2)	297(2)	173(1)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	11.3936(13)	10.5085(12)	10.1328(4)
b, Å	10.3025(13)	13.189(2)	13.2837(5)
c, Å	18.011(2)	13.3900(13)	13.3970(5)
α, deg	90	116.356(9)	116.128(1)
β, deg	104.785(9)	94.354(9)	94.243(1)
γ, deg	90	102.041(11)	101.490(1)
V, Å^3	2044.2(4)	1595.9(3)	1559.5(1)
Z	4	2	2
ρ_{calcd}, g/cm^3	1.450	2.277	2.373
μ, mm^{-1}	1.645	9.458	9.745
F(000)	896	996	1016
Crystal shape (size, mm);	Prism (0.30 × 0.20 × 0.18)	Prism (0.45 × 0.18 × 0.18)	Prism (0.31 × 0.19 × 0.16)
θ range, deg	2.30–28.00	2.02–27.50	2.86–31.49
Reflection index range	$0 \le h \le 15$, $-13 \le k \le 0$, $-23 \le l \le 23$	$0 \le h \le 13$, $-15 \le k \le 14$, $-17 \le l \le 17$	$-7 \le h \le 14$, $-19 \le k \le 18$, $-18 \le l \le 19$
Measured reflections	5164	7365	12922
Independent reflections	4927 (R_{int} = 0.0280)	6969 (R_{int} = 0.0311)	9569 (R_{int} = 0.0279)
Variable parameters	226	290	292
Goodness-of-fit	1.017	1.056	1.010
R factors for $F^2 > 2\sigma(F^2)$	R_1 = 0.0376, wR_2 = 0.0854	R_1 = 0.0413, wR_2 = 0.1041	R_1 = 0.0344, wR_2 = 0.0891
R factors for all reflections	R_1 = 0.0596, wR_2 = 0.0942	R_1 = 0.0484, wR_2 = 0.1083	R_1 = 0.0413, wR_2 = 0.0928
Extinction coefficient	Was not determined	0.0035(2)	Was not refined
Residual electron density (min/max), *e* Å^{-3}	–0.427/0.621	–1.719/2.779	–3.114/1.909

Selected crystallographic data and refinement results for structures **I–III** are presented in Table 1. Selected bond lengths and bond angles are given in Table 2. The coordinates of atoms and other parameters of compounds **I–III** were deposited with the Cambridge Structural Data Base (nos. 686466–686468).

Table 2. Bond lengths and bond angles in structures **I–III**

Bond	*d*, Å	Angle	ω, deg
		I	
P(1)–C(11)	1.790(3)	C(11)P(1)C(5)	108.50(16)
P(1)–C(5)	1.795(3)	C(11)P(1)C(1)	108.87(15)
P(1)–C(1)	1.796(3)	C(5)P(1)C(1)	111.07(15)
P(1)–C(17)	1.796(3)	C(11)P(1)C(17)	110.80(15)
C(1)–C(2)	1.517(4)	C(5)P(1)C(17)	106.29(15)
C(2)–C(3)	1.502(4)	C(1)P(1)C(17)	111.26(16)
C(2)–C(31)	1.549(9)	C(2)C(1)P(1)	114.5(2)
C(3)–C(4)	1.500(4)	C(3)C(2)C(1)	117.6(4)
C(31)–C(41)	1.509(10)	C(3)C(2)C(31)	29.4(8)
C(5)–C(10)	1.379(5)	C(1)C(2)C(31)	97.6(7)
		II	
Bi(1)–O(1*A*)	2.747(6)	O(1*A*)Bi(1)I(2)	171.360(14)
Bi(1)–I(2)	2.8531(7)	O(1*A*)Bi(1)I(4)	83.070(13)
Bi(1)–I(4)	2.9260(7)	I(2)Bi(1)I(4)	93.82(3)
Bi(1)–I(3)	2.9953(6)	O(1*A*)Bi(1)I(3)	93.56(15)
Bi(1)–I(1)	3.1508(7)	I(2)Bi(1)I(3)	94.762(19)
Bi(1)–I(1*A*)	3.2824(8)	I(4)Bi(1)I(3)	95.55(2)
P(1)–C(11)	1.795(7)	O(1*A*)Bi(1)I(1)	80.48(15)
P(1)–C(5)	1.798(7)	I(2)Bi(1)I(1)	91.65(2)
P(1)–C(1)	1.800(7)	I(4)Bi(1)I(1)	92.60(2)
P(1)–C(17)	1.806(7)	I(3)Bi(1)I(1)	169.263(16)
O(1A)–C(1*A*)	1.202(10)	O(1*A*)Bi(1)I(1*A*)	91.27(13)
C(1A)–C(3*A*)	1.456(13)	I(2)Bi(1)I(1*A*)	91.59(2)
C(1A)–C(2*A*)	1.498(12)	I(4)Bi(1)I(1*A*)	174.170(19)

Symmetry transformation: (*Ä*) $-x-1, -y, -z+1$.

		III	
Bi–O	2.507(3)	OBiI(2)	176.49(7)
Bi–I(2)	2.8984(3)	OBiI(3)	84.95(6)
Bi–I(3)	2.9206(3)	I(2)BiI(3)	91.592(9)
Bi–I(4)	2.9786(3)	OBiI(4)	86.61(7)
Bi–I(1*A*)	3.1961(3)	I(2)BiI(4)	94.419(8)
Bi–I(1)	3.3108(3)	I(3)BiI(4)	97.033(8)
S–O	1.519(2)	OBiI(1*A*)	82.22(7)
S–C(2)	1.761(5)	I(2)BiI(1*A*)	97.339(8)
S–C(1)	1.777(4)	I(3)BiI(1*A*)	92.096(8)
P–C(31)	1.793(4)	I(4)BiI(1*A*)	164.896(7)
P–C(21)	1.795(3)	OBiI(1)	87.28(6)
P–C(11)	1.800(3)	I(2)BiI(1)	96.146(8)
P–C(3)	1.805(4)	I(3)BiI(1)	171.621(8)
C(3)–C(4)	1.532(5)	I(4)BiI(1)	85.597(7)
C(4)–C(5)	1.531(5)	I(1*A*)BiI(1)	83.752(7)
C(5)–C(6)	1.536(6)	Bi(*A*)I(1)Bi	96.248(7)
		OSC(2)	104.4(2)
		OSC(1)	104.2(2)
		C(2)SC(1)	98.0(3)
		C(31)PC(21)	107.2(2)
		C(31)PC(11)	109.0(2)
		C(21)PC(11)	108.9(2)
		C(31)PC(3)	108.1(2)
		C(21)PC(3)	112.0(2)
		C(11)PC(3)	111.5(2)
		SOBi	117.1(1)

Symmetry transformation: (*Ä*) $-x, -y+1, -z$.

RESULTS AND DISCUSSION

The bismuth(III) atom is prone to the formation of bi-, tetra-, hexa-, and octanuclear anions with inorganic ligands, which often perform different structural functions [1, 2, 5–7]. The complexes are synthesized, as a rule, from the onium compounds and predominantly from bismuth iodide. We continued to study similar reactions, taking triphenyl(*n*-butyl)phosphonium iodide (**I**) as one of the starting reactants.

According to the X-ray diffraction data, crystal **I** consists of somewhat distorted tetrahedral triphenyl(*n*-butyl)phosphonium cations (CPC angles 106.3(2)°–111.3(2)°) and iodide anions (Fig. 1). The butyl substituent in crystal **I** is disordered over two positions: the methyl group exists in the synclinal (74%) and antiperiplanar (26%) conformations.

The interaction of complex **I** with an equimolar amount of bismuth iodide in acetone afforded complex **II** containing the binuclear anions with the coordinated acetone molecules

$$\underset{\textbf{(I)}}{2[Ph_3BuP]^+I^-} + 2BiI_3 \xrightarrow{Me_2C=O} \xrightarrow{Me_2C=O} \underset{\textbf{(II)}}{[Ph_3BuP]_2^+[Bi_2I_8 \cdot 2Me_2CO]^{2-}}.$$

A crystal of complex **II** consists of the tetrahedral triphenyl(*n*-butyl)phosphonium cations (CPC angles 107.8(3)°–112.0(3)°). The P–C_{Bu} (1.800(7) Å) and P–C_{Ph} (1.795(7)–1.806(7) Å) spacings in complex **II** are compared with analogous bond lengths in complex **I** (P–C_{Bu} 1.796(3), P–C_{Ph} 1.790(3)–1.796(3) Å). In the centrosymmetric anion of complex **II**, the octahedral coordinated bismuth atoms are linked in pairs by two bridging (br) iodine atoms (Bi–I_{br} 3.1508(7) and 3.2824(8) Å), which are coplanar to four terminal (t) iodine atoms (Bi–I_t 2.9260(7) and 2.9953(6) Å) (Fig. 2). The Bi(1) atom deviates by 0.162 Å from the equatorial plane of the I(1), I(1*A*), I(3), and I(4) atoms to the I(2) atom. The Bi–O spacing in complex **II** (2.747(6) Å) is longer than that in a similar bis(tetraiodobismuth) dianion coordinated by tetrahedrofuran (B–O 2.638 Å) [8]. The central square tetraatomic Bi_2I_2 cycle is somewhat distorted (the $BiI_{br}Bi$ and $I_{br}BiI_{br}$ angles are 94.92(2)° and 85.08(2)°, respectively), and the largest IBiI angle (95.55(2)°) is observed for the terminal iodine atoms. The O(1*A*)Bi(1)I(2), I(4)Bi(1)I(1*A*), and I(1)Bi(1)I(3) diagonal angles are 171.360(14)°, 174.170(19)°, and 169.263(16)°, respectively.

The interaction of equimolar amounts of complex **I** and bismuth iodide in dimethyl sulfoxide (DMSO) afforded analogous complex **III**, which differed from

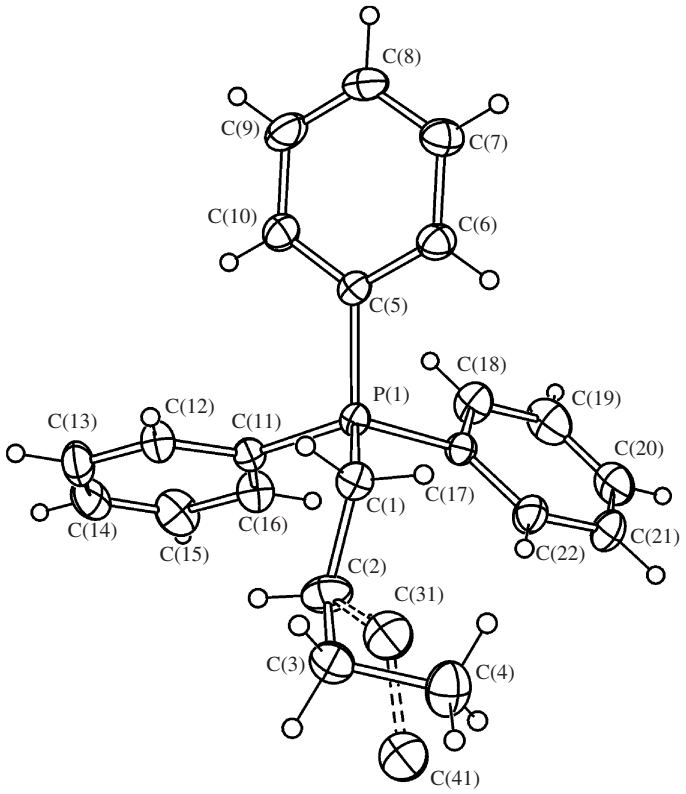

Fig. 1. Structure of the organic cation in compound **I**.

complex **II** only by the solvent molecules coordinated at the bismuth atoms:

$$2[Ph_3BuP]^+I^- + 2BiI_3 \xrightarrow{DMSO} \xrightarrow{DMSO} [Ph_3BuP]_2^+[Bi_2I_8 \cdot 2ДМСО]^{2-}.$$

(**III**)

Complex **III**, as complex **II**, is resistant to moisture and air oxygen, has a distinct melting point, and is well soluble in organic solvents. The geometric parameters of the tetrahedral cation of complex **III** (CPC angles 107.2(2)°–112.0(2)°; spacings P–C_{Bu} 1.805(4), P–C_{Ph} (1.793(4)–1.800(3) Å) are similar to those found in complex **II**. In cations **II** and **III**, the butyl fragments exist in the synclinal conformation. The six iodine atoms and two bismuth atoms of the centrosymmetric anion lie approximately in the same plane, the iodine atom and dimethyl sulfoxide molecule being arranged at each side of the plane (Fig. 3). The bismuth atom has a coordination of a distorted octahedron (the OBiI(2), I(4)BiI(1*A*)', and I(3)BiI(1) angles are 176.49(7)°, 164.896(7)°, and 171.62(8)°, respectively). The Bi–O bond in crystal **III** 2.507(3) Å) is stronger than a similar bond in complex **II** (2.747(6) Å), possibly, due to a higher donating ability of DMSO compared with that of acetone. The spacings between the bismuth atoms and bridging iodine atoms in complex **III** (Bi–I_{br} 3.1961(3) and 3.3108(3) Å) are somewhat longer than those in complex **II** (Bi–I_{br} 3.1508(7) and 3.2824(8) Å). The Bi–I_t bonds to the I(3) and I(4) atoms in the *trans*-positions to the I_{br} atoms, on the contrary, in complex **III** (2.9496(3) ± 0.0290 Å) are somewhat shorter, on the average, than those in complex **II** (2.9607(7) ± 0.0347 Å). The I(2) terminal atom existing in front of the solvent molecule in complex **III** is remote from the central atom by 2.8984(3) Å, which is longer than a similar distance in complex **II** (Bi–I(2) 2.8531(2) Å).

Thus, the reactions of equimolar amounts of bismuth(III) iodide with triphenyl(*n*-butyl)phosphonium iodide in acetone or dimethyl sulfoxide afford the bismuth complexes with the $[Bi_2I_8 \cdot 2Solv]^{2-}$ anions in which an insignificant difference of the bond lengths and bond angles at the bismuth atoms is due to the nature of the organic ligand.

ACKNOWLEDGMENTS

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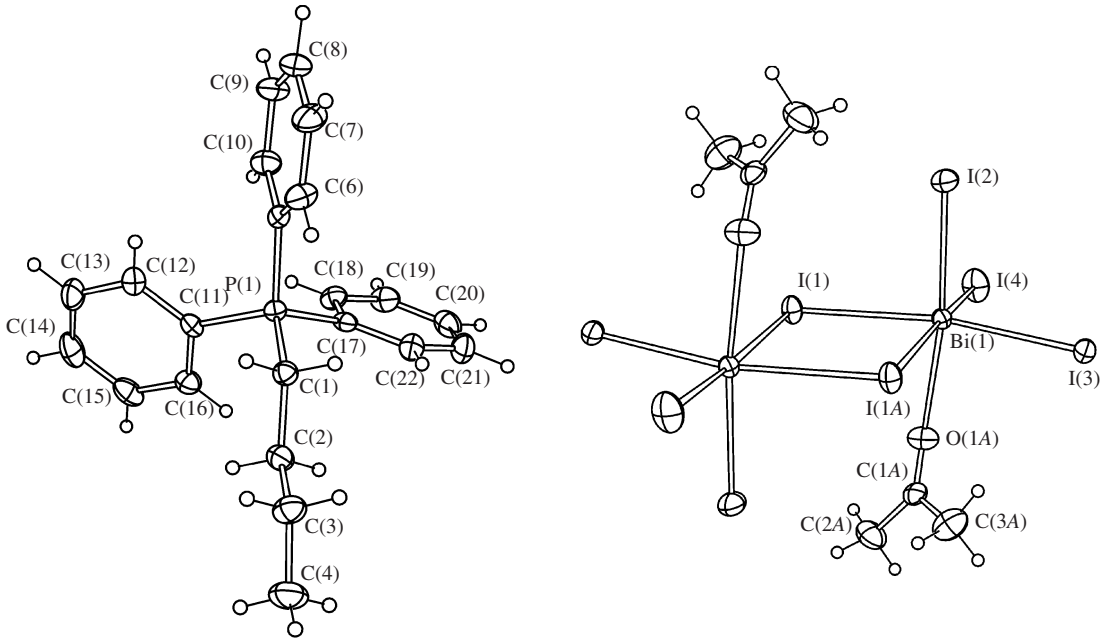

Fig. 2. Structures of the cation and anion in compound **II**.

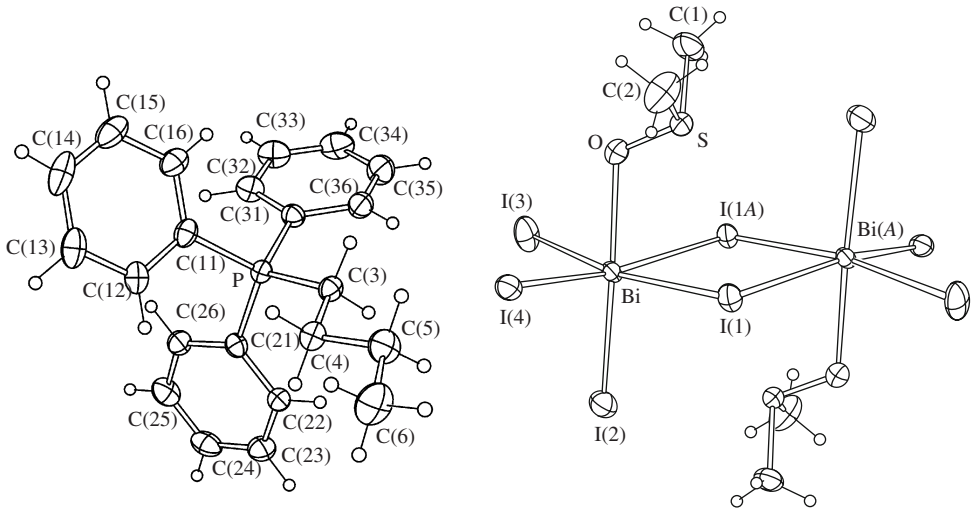

Fig. 3. Structures of the cation and anion in compound **III**.

M.A. Pushilin for performing X-ray diffraction analysis of complex **III**.

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