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Synthesis and Structure of Bismuth Complexes $[Ph_4P]_4[Bi_8I_{28}]$, $[Ph_4P]_2[Bi_2I_8{\cdot}2Me_2S{=}O]{\cdot}2Me_2S{=}O$, $[(Me_2S{=}O)_8Bi][Bi_2I_9]$

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Abstract—Complexes $[Ph_4P]_2[Bi_2I_8(Me_2S{=}O)_2]{\cdot}2Me_2S{=}O$ (**I**) and $[Ph_4P]_4[Bi_8I_{28}]$ (**II**) were obtained by the reaction of tetraphenylphosphonium iodide with bismuth triiodide in DMSO and acetone, respectively. Dissolving bismith iodide in DMSO resulted in the formation of complex $[(Me_2S{=}O)_8Bi][Bi_2I_9]$ (**III**). Reactions of complexes **II** or **III** with tetraphenylphosphonium iodide in DMSO yielded complex **I**. The structure of the obtained bismuth complexes was confirmed by X-ray diffraction data.

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Composition of complexes formed in the reactions of stibonium, phosphonium, and ammonium iodides with bismuth triiodide, as well as the design of I,Bi-containing anions, which may include from 1 to 8 bismuth atoms, depend on the nature of the initial salt, the reagents ratio, and the solvent nature [1].

To determine the effect of the solvent nature on the complex structure we performed a systematic study of the reactions of bismuth triiodide with tetraphenylphosphonium iodide in dimethyl sulfoxide. Previously in the reaction of bismuth triiodide with tetraphenylphosphonium iodide at a molar ratio of 2:1 in dimethyl sulfoxide the $[Ph_4P]_2[BiI_5{\cdot}Me_2S{=}O]$ complex has been isolated, where a solvent molecule is included into the coordination sphere of the metal in the anion [2].

We investigated the reactions of these compounds in the molar ratios of 1:1, 1:1.5, 1:2 and found that in all cases the complex has the same structure, $[Ph_4P]_2Bi_2I_8(Me_2S{=}O)_2]{\cdot}2Me_2S{=}O$ **I**, i. e., increasing concentration of bismuth triiodide does not result complication of the anion. A similar result was obtained in the reaction of bismuth triiodide with triphenylalkylphosphonium iodide in dimethyl sulfoxide [1].

$$2Ph_4PI + 2BiI_3 \xrightarrow{Me_2S=O} [Ph_4P]_2[Bi_2I_8(Me_2S{=}O)_2]{\cdot}2Me_2S{=}O$$
I

At the same time triphenyl(isoamyl)phosphonium iodide is known to react with bismuth triiodide (1–2 mol) in acetone to form a complex with an eight-metal anion $[Ph_3(isoamyl)P]_4[Bi_8I_{28}]$ [3]. Complex $[Ph_4P]_4[Bi_8I_{28}]$ (**II**) was similarly obtained.

$$4[Ph_4P]I + 8\,BiI_3 \longrightarrow [Ph_4P]_4[Bi_8I_{28}]$$
II

Complex **II** was found to react with tetraphenylphosphonium iodide (1:4 mol) in DMSO solution to form complex **I**.

$$[Ph_4P]_4[Bi_8I_{28}] + 4Ph_4PI \xrightarrow{Me_2S=O} 4[Ph_4P]_2[Bi_2I_8(Me_2S{=}O)_2]{\cdot}2Me_2S{=}O$$
I

Dimethyl sulfoxide is an aprotic polar solvent. Its polarity determines the basic properties and the ability to solvate cations. It was found that the reaction of DMSO with bismuth triiodide is not limited to solvation of the bismuth cation in the solution. After removing a part of the solvent, the orange crystals of the ionic complex with the binuclear anion $[(Me_2S{=}O)_8Bi]{\cdot}[Bi_2I_9]$ (**III**) precipitate. Complex **III** is sensitive to the action of moisture.

$$3BiI_3 + 8Me_2S{=}O \longrightarrow [(Me_2S{=}O)_8Bi][Bi_2I_9]$$
III

The reaction of complex **III** with tetraphenylphosphonium iodide in dimethyl sulfoxide also leads to the formation of compound **I** in 98% yield.

$$2[(Me_2S{=}O)_8Bi][Bi_2I_9] + 6Ph_4PI \rightarrow 3[Ph_4P]_2[Bi_2I_8(Me_2S{=}O)_2]\cdot 2Me_2S{=}O.$$

Thus, bismuth triiodide reacts with dimethylsulfoxide to form ionic complex **III**, which transforms into more stable complex **I** at adding tetraphenylphosphonium iodide.

By the X-ray diffraction data, the crystal of complex **I** contains tetrahedral tetraphenylphosphonium cations [CPC angles 107.3(1)°–111.5(1)°]. The P–C distances are 1.789(3)–1.800(3) Å. In the centrosymmetric anion $[Bi_2I_8(Me_2S{=}O)_2]^{2-}$ the bismuth atoms have a distorted octahedral coordination. Equatorial positions are occupied by four iodine atoms, two of which are bidentate bridging (I^4, I^{4a}) and two others are monodentate terminal (I^1, I^2) atoms. Axial positions are occupied by an iodine atom (I^3) and oxygen atom of $Me_2S{=}O$ molecule (Fig. 1). Diagonal angles $O^1Bi^1I^3$, $I^1Bi^1I^{4a}$, $I^2Bi^1I^4$ are 173.23(5)°, 174.684(6)° and 166.280(6)°, respectively. The four-membered ring $[Bi_2I_2]$ is virtually flat. The angles $Bi^1I^4Bi^{1a}$ and $I^4Bi^1I^{4a}$ are 100.551(6)° and 79.448(6)°, respectively. Organic ligands are *trans*-located relative to the ring plane. The distances Bi^1–I^4 [3.2209(2) Å] and Bi^1–I^{4a} [3.3402(2) Å] are longer than Bi^1–I^1, Bi^1–I^2 and Bi^1–I^3 [2.9211(2), 2.9515(2) and 2.9511(2) Å]. The Bi^1–O^1 bond length [2.558(2) Å] is less than that in the bis(tetraiodobismuth) dianion coordinated with THF (Bi–O 2.638 Å) [4]. Interaction with the bismuth atom causes a lengthening of S=O bond [1.527(2) Å] in the bonded molecule, compared with the DMSO solvate [1.491(3) Å]. The average S–C bond lengths [1.773(3) Å] in the coordinated molecule and in the solvate [1.778(4) Å] are almost identical.

The structural organization in the crystal of **I** is mainly caused by the weak intermolecular hydrogen bonding. Thus, two cations are related to each other through two solvate molecules of dimethyl sulfoxide, which serve as bridges: the distances C^{45}–$H^{45a}\cdots O^2$ and C^{32}–$H^{32a}\cdots O^2$ are 2.30 and 2.50 Å, respectively (Fig. 2). The anions form a chain through the contacts C^2–$H\cdots I^4$ (3.05 Å). The weak interactions C^{43}–$H^{43a}\cdots I^4$ (3.15 Å) and C^{25}–$H^{25a}\cdots I^2$ (3.16 Å) between the anions and cations are observed.

In the $[(Me_2S{=}O)_8Bi]^{3+}$ cation of the complex **III** eight molecules of DMSO are coordinated with the bismuth cation through the oxygen atoms [Bi^2–O

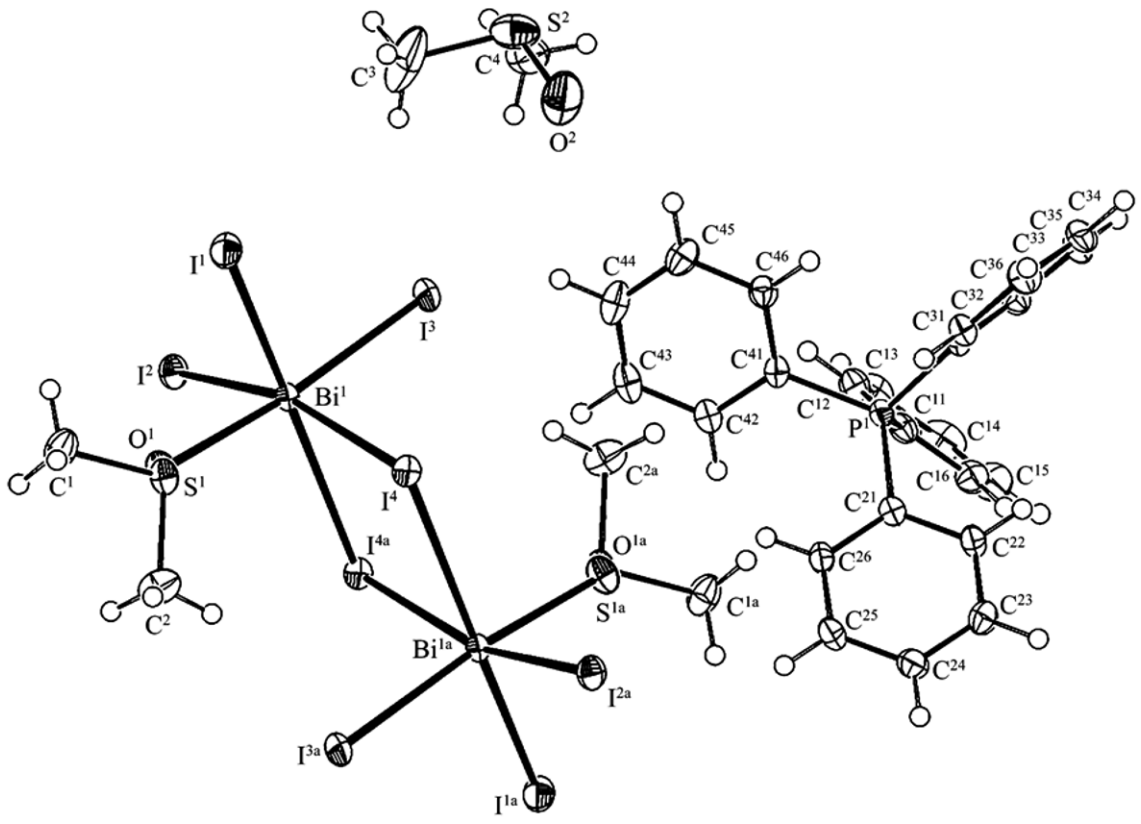

Fig. 1. General view of the molecule of complex **I**.

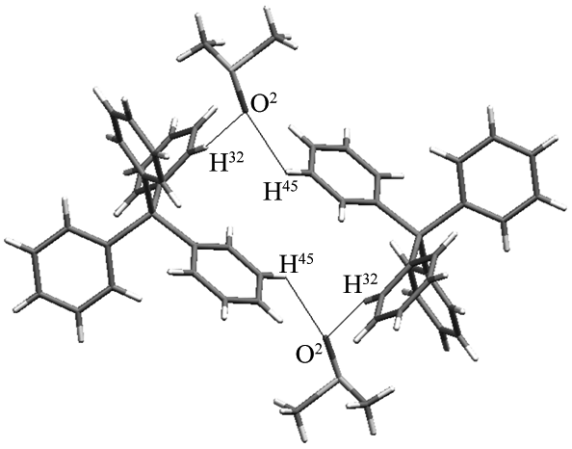

Fig. 2. Structural organization of the cations in the crystal of **I**.

2.365(6)–2.509(6) Å], angles OBiO vary in the range 68.8(2)°–100.6(3)° (Fig. 3). The S=O bond lengths in DMSO molecules vary in the range 1.196(9)–1.517(6) Å, while the correlation between the strength of binding of oxygen and bismuth cation and the length of S=O bond is not observed. So, at almost the same distances Bi^2–O^4 [2.444(6) Å] and Bi^2–O^3 [2.449(7) Å] the S=O bond lengths in the corresponding molecules equal 1.475(8) and 1.250(8) Å. In the anion $[Bi_2I_9]^{3-}$ the bismuth atoms have octahedral coordination. The fragments BiI_3, bonded via three bridging iodine atoms (I^6, I^7, I^8), have virtually eclipsed conformations. Three four-membered metallocycles $[Bi_2I_2]$ have the inflection lines on the Bi^1 –Bi^3 diagonal. The *trans*-angles in the octahedral environment of the bismuth atoms Bi^1 and Bi^3 are in the ranges 170.63(2)°–173.36(2)° and 169.73(2)°–171.44(2)°. The distances Bi^1–$I^{6,7,8}$ and Bi^3–$I^{6,7,8}$ are 3.1650(7), 3.2404(7), 3.2376(7) and 3.3549(8), 3.2812(7), 3.1623(7) Å, respectively. The Bi^1–$I^{2,5,9}$ and Bi^3–$I^{1,3,4}$ bonds are shorter: 2.9756(7), 3.0206(7), 2.9937(7) and 2.9391(7), 2.9200(8), 3.0231(7) Å, respectively.

In the crystal **III** the anions are isolated. The cations are bondend via a weak hydrogen bond C^{11}–$H^{11c}\cdots O^6$ (2.69 Å) (Fig. 4). There are C^2–$H^{2a}\cdots I^5$ (3.12 Å) interactions between the cations and anions. Thus, the reaction of bismuth triiodide with tetraphenylphosphonium iodide regardless of the molar ratio (1:1, 1:1.5, 1:2) in DMSO is always accompanied by the formation of the complex $[Ph_4P]_2[Bi_2I_8\cdot 2Me_2S{=}O]\cdot 2Me_2S{=}O$, whose structure is obviously the most energetically favorable. This is confirmed by the observed anion rearrangement in $[Ph_4P]_4[Bi_8I_{28}]$ and $[(Me_2S{=}O)_8Bi][Bi_2I_9]$ complexes, when tetraphenylphosphonium iodide was added to their DMSO solutions.

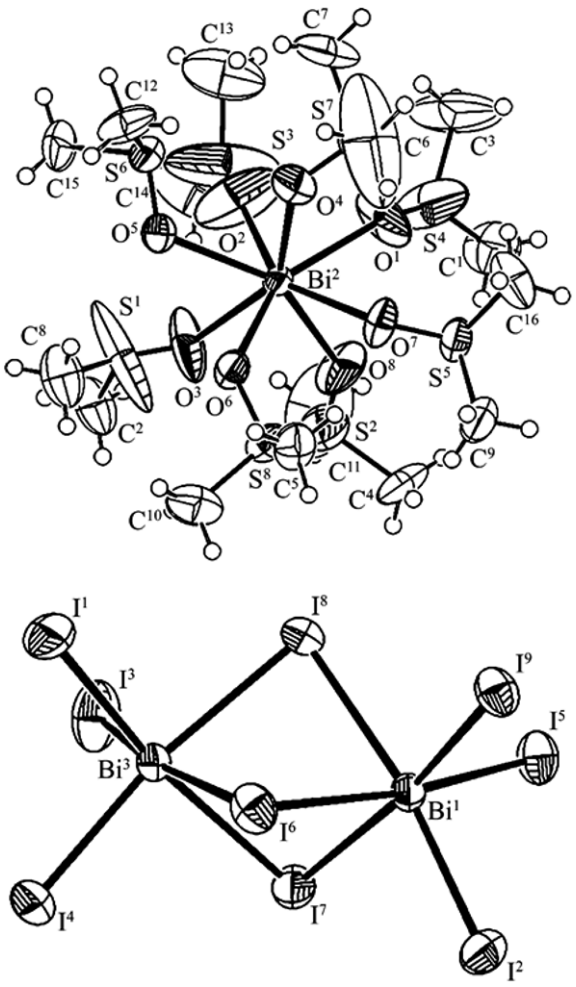

Fig. 3. General view of the molecule of complex **III**.

EXPERIMENTAL

The IR spectra were recorded on a 1201 IR Fourier spectrometer from KBr pellets. The X-ray diffraction analysis of the crystals **I** and **III** was performed on a Bruker P4 diffractometer (MoK_α-radiation, λ 0.71073 Å, graphite monochromator). Data collecting and editing, and refinement of the unit cell parameters, as well as the accounting for extinction, were performed using SMART and SAINT-Plus programs [5]. All the calculations were made by SHELXL/PC program [6]. The structure was determined by the direct method and refined by the least-squares method in anisotropic approximation for the nonhydrogen atoms.

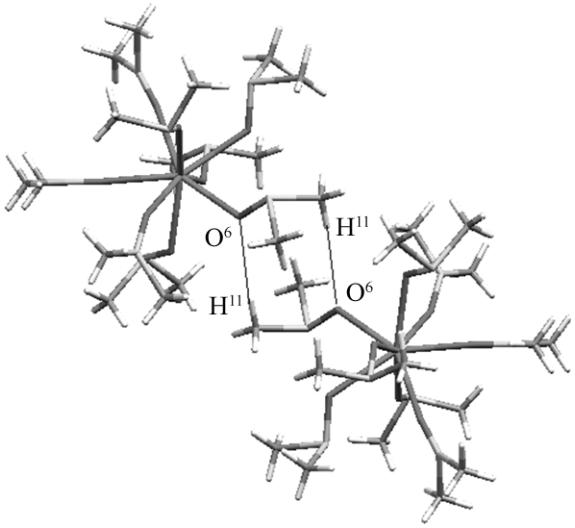

Fig. 4. Structural organization of the cations in the crystal of **III**.

The main crystallographic data of the structures **I** and **III** are given in Table 1, the main bond lengths and angles, in Table 2.

Synthesis of $[Ph_4P]_2[Bi_2I_8 \cdot 2Me_2S{=}O] \cdot 2Me_2S{=}O$ complex (I). *a*. A mixture of 0.50 g (1.07 mmol) of tetraphenylphosphonium iodide, 0.63 g (1.07 mmol) of bismuth triiodide, and 5 ml of DMSO was stirred to dissolve the starting reagents. The orange solution was concentrated, the crystals were filtered off and dried. Yield 1.14 g (88%), mp 108°C. IR spectrum, ν, cm^{-1}: 419, 526, 689, 721, 943, 986, 1048, 1105, 1434, 1439, 1636, 2984. Found, %: C 27.57; H 2.77. $C_{56}H_{64}O_4Bi_2I_8P_2S_4$. Calculated, %: C 27.73; H 2.64.

b. A mixture of 1.77 g (0.27 mmol) of compound **II** and 0.50 g (1.07 mmol) of tetraphenylphosphonium iodide in 5 ml of DMSO was stirred at 20°C. The orange solution was concentrated, the crystals were filtered off and dried. Yield 2.36 g (97%), mp 108°C.

c. A mixture of 0.22 g (0.09 mmol) of compound **III** and 0.13 g (0.27 mmol) of tetraphenylphosphonium iodide in 5 ml of dimethyl sulfoxide was stirred until complete dissolution of the reactants. Then the solvent was removed. Yield 0.33 g (98%), mp 108°C. The IR spectrum is identical to that of the compound obtained via the reaction of complex **II** with tetraphenylphosphonium iodide (1:4 mol) and bismuth triiodide with tetraphenylphosphonium iodide (1:1 mol) in dimethyl sulfoxide.

Synthesis of $[Ph_4P]_4[Bi_8I_{28}]$ complex (II). To a solution of 1.27 g (2.15 mmol) of bismuth triiodide in acetone was added a solution of 0.50 g (1.07 mmol) of tetraphenylphosphonium iodide in 20 ml of acetone. The red solution was concentrated, the crystals were filtered off and dried. Yield 1.73 g (98%), decomposition point 230°C. IR spectrum, ν, cm^{-1}: 521, 528, 686, 717, 723, 746, 997, 1105, 1162, 1182, 1188, 1432, 1437, 1480, 2987. Found, %: C 17.31; H 1.13. $C_{96}H_{80}Bi_8I_{28}P_4$. Calculated, %: C 17.50; H 1.22.

Table 1. Crystallographic data and experimental parameters for the structure of compounds **I** and **III**

Parameter	Value	
	I	**III**
M	2424.41	2346.18
T, K	150	293(2)
Crystal structure	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.3599(2)	12.4505(6)
b, Å	13.9974(3)	14.9701(7)
c, Å	15.5120(3)	16.5126(8)
α, deg	112.9560(10)	79.129(4)
β, deg	91.6700(10)	73.208(4)
γ, deg	105.3760(10)	74.782(4)
V, $Å^3$	1784.14(6)	2821.9(2)
Z	1	2
d_{calc}, g cm^{-3}	2.256	2.761
μ, mm^{-1}	8.587	14.577
F(000)	1116	2029
Crystal form (size, mm)	Fragment (0.32×0.25×0.16)	Prism (0.34×0.21×0.13)
Range of the data collection by θ, deg	2.02–27.50	6.54–30.51
R of reflections indices	$-11 \le h \le 12$, $-19 \le k \le 18$, $-22 \le l \le 16$	$-17 \le h \le 17$ $-21 \le k \le 19$ $-22 \le l \le 23$
Reflections measured	21033	30380
Independent reflections	9534 (R_{int} 0.0311)	7719 (R_{int} 0.043)
Refined parameters	348	397
GOOF	1.023	0.864
R-Factors for $F^2 > 2\sigma(F^2)$	R_1 0.0208, wR_2 0.0381	R_1 0.0524 wR_1 0.0872
R-Factors for all reflections	R_1 0.0268, wR_2 0.0398	R_1 0.1258 wR_1 0.0953
Residual electron density (min/max), *e* $Å^{-3}$	0.841/–0.977	–4.276/4.067

Table 2. Bonds lengthes and bond angles in structures **I** and **III**

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
				I			
$Bi^1–I^1$	2.9211(2)	$I^1Bi^1I^2$	95.742(6)	$S^1–O^1$	1.5273(19)	$O^1Bi^1I^1$	82.29(5)
$Bi^1–I^2$	2.9515(2)	$I^1Bi^1I^3$	90.967(7)	$S^1–C^1$	1.778(3)	$O^1Bi^1I^3$	173.23(5)
$Bi^1–I^3$	2.9511(2)	$I^1Bi^1I^4$	96.013(7)	$S^1–C^2$	1.769(3)	$O^1Bi^1I^{4\#1}$	94.70(5)
$Bi^1–I^4$	3.2209(2)	$I^1Bi^1I^{4\#1}$	174.684(6)	$P^1–C^{11}$	1.800(3)	$Bi^1I^4Bi^{1\#1}$	100.551(6)
$Bi^1–I^{4\#1}$	3.3402(2)	$I^2Bi^1I^4$	166.280(6)	$P^1–C^{21}$	1.796(3)	$C^{31}P^1C^{21}$	107.31(12)
$Bi^1–O^1$	2.5578(19)	$I^3Bi^1I^2$	94.458(7)	$P^1–C^{31}$	1.790(3)	$C^{41}P^1C^{11}$	107.44(13)
$I^4–Bi^{1\#}$	3.3402(2)	$I^4Bi^1I^{4\#1}$	79.448(6)	$P^1–C^{41}$	1.789(3)	$C^{41}P^1C^{31}$	111.50(13)
				III			
$Bi^1–I^2$	2.9756(7)	$I^6Bi^1I^8$	81.99(2)	$Bi^2–O^2$	2.460(8)	$O^6Bi^2O^3$	76.8(3)
$Bi^1–I^9$	2.9937(7)	$I^5Bi^1I^8$	88.91(2)	$Bi^2–O^5$	2.505(6)	$O^8Bi^2O^6$	92.7(2)
$Bi^1–I^5$	3.0206(7)	$I^9Bi^1I^6$	90.14(2)	$Bi^2–O^7$	2.509(6)	$O^4Bi^2O^2$	93.9(3)
$Bi^1–I^6$	3.1650(7)	$I^9Bi^1I^5$	92.76(2)	$Bi^3–I^3$	2.9200(8)	$O^6Bi^2O^4$	96.7(2)
$Bi^1–I^8$	3.2376(7)	$I^2Bi^1I^5$	94.41(2)	$Bi^3–I^1$	2.9391(7)	$O^8Bi^2O^2$	100.6(3)
$Bi^1–I^7$	3.2404(7)	$I^5Bi^1I^6$	170.63(2)	$Bi^3–I^4$	3.0231(7)	$O^1Bi^2O^3$	126.3(3)
$Bi^2–O^8$	2.365(6)	$I^2Bi^1I^8$	170.89(2)	$Bi^3–I^8$	3.1623(7)	$O^6Bi^2O^2$	141.3(4)
$Bi^2–O^6$	2.405(5)	$I^9Bi^1I^7$	173.36(2)	$Bi^3–I^7$	3.2812(7)	$O^8Bi^2O^4$	143.2(3)
$Bi^2–O^1$	2.434(7)	$O^1Bi^2O^2$	71.9(4)	$Bi^3–I^6$	3.3549(8)	$O^6Bi^2O^1$	146.8(3)
$Bi^2–O^4$	2.444(6)	$O^8Bi^2O^3$	73.3(3)	$S^1–O^3$	1.250(8)	$O^4Bi^2O^3$	143.5(3)
$Bi^2–O^3$	2.449(7)	$O^8Bi^2O^1$	75.1(3)	$S^1–C^8$	1.651(11)	$O^8Bi^2O^5$	147.6(2)

Synthesis of $[(Me_2S=O)_8Bi][Bi_2I_9]$ complex (III). 0.25 g (0.42 mmol) of bismuth triiodide was dissolved in 10 ml of DMSO. The resulting yellow-orange solution was concentrated, the crystals were filtered off and dried. Yield 0.32 g (97%), mp 68°C. IR spectrum, ν, cm^{-1}: 667, 707, 916, 975, 1025, 1310, 1404, 2908, 2992. Found, %: C 7.96; H 1.81. $C_{16}H_{48}O_8I_9S_8Bi_3$. Calculated, %: C 08.02; H 2.01.

REFERENCES

1. Klepikov, N.N., *Candidate Sci. (Chem.) Dissertation*, Vladivostok, 2009.
2. Sharutin, V.V., Yegorova, I.V., Sharutina, O.K., Dorofeeva, O.A., Molokov, A.A., and Fukin, G.K., *Koord. Khim*., 2005, vol. 31, no. 10, p. 791.
3. Sharutin, V.V., Yegorova, I.V., Klepikov, N.N., Boyarkina, E.A., and Sharutina, O.K., *Zh. Neorg. Khim.,* 2009, vol. 54, no. 11, p. 1847.
4. Krautscheid, H., *Z. Anorg. Allg. Chem*.,1999, vol. 625, p. 192.
5. *Bruker (2000) SMART, Bruker Molecular Analysis Research Tool,* Versions 5.625 Bruker AXS, Madison, Wisconsin, USA.
6. *Bruker (2000) SAINTPlus Data Reduction and Correction Program*, Versions 6.02a, Bruker AXS, Madison, Wisconsin, USA.