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Synthesis and Structure of Phenylbismuth Bis(4-nitrophenyl)acetate and Diphenylbismuth 2-Nitrobenzoate

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Abstract—Reaction of triphenylbismuth with 4-nitrophenylacetic and 2-nitrobenzoic acids provided phenylbismuth bis(4-nitrophenyl)acetate and diphenylbismuth 2-nitrobenzoate. According to the XRD data, bismuth atoms have distorted octahedral and trigonal-bipyramid coordinations. Tridentate carboxylate ligands play role of chelates.

Keywords: phenylbismuth bis(4-nitrophenyl)acetate, diphenylbismuth 2-nitrobenzoate, X-ray analysis

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An interest to investigation of the synthetic approaches to bismuth carboxylates is explained by their use as precursors to finely crystalline bismuth oxide, heterometallic bismuth-contained oxides for segnetoelectric materials and catalysts [1, 2], and as biologically active compounds [3–6].

One of the main synthetic approaches to bismuth carboxylates BiX_3, $PhBiX_2$, Ph_2BiX [X = OC(O)R] is the reaction of triphenylbismuth with a carboxylic acid. The completeness of the phenyl group substitution is determined by the molar ratio of the reagents, nature of an acid and a solvent, and solubility of the formed carboxylates.

In solutions or in melt at molar (here and further) ratio of triphenylbismuth and an acid as 1 : 3 or at acid excess a rupture of all bonds Bi–Ph happened in a majority of cases, and the formation of bismuth tricarboxylate occurred [7, 8].

Whatever the ratio of triphenylbismuth and chloro- or bromoacetic acid are, the reaction of triphenylbismuth with halocarboxylic acids in chloroform includes elimination of all the phenyl groups and the formation of $[BiX_3]_n$ [9]. When toluene was used as a solvent, a mixture of carboxylates with the prevalence of $PhBiX_2$ (the reagents ratio of 1 : 1 or 1 : 2), or BiX_3 (at the ratio 1 : 3) formed. The reaction of triphenylbismuth with 3,4,5-$F_3C_6H_2C(O)OH$ in toluene, benzene, or *p*-xylene in the presence of air oxygen at any ratio of the reagents proceeded with rupture of all Bi–Ph bonds to form the tetranuclear carboxylate $Bi_4O_2X_8$ solvated with a solvent molecule. In *o*- and *m*-xylene the reaction resulted in the rupture of two Bi–Ph bonds and the formation of a dimer $[PhBiX_2]_2$. Phenylbismuth dicarboxylate formed in the reactions with salicylic, 2-hydroxy-4-methylbenzoic (ratio of 1 : 2, boiling acetone, 4 h) [10], pyridine-2-carboxylic (ratio of 1 : 3, toluene, 10–12 h) [8], pyrazine-2-carboxylic, quinoline-2-carboxylic, and 3-hydroxypyridine-2-carboxylic (ratio of 1 : 3, ethanol, 6–12 h) acids [11]; however, the reactions with furan-2-carboxylic (ratio of 1 : 3, ethanol, 12–14 h) and 2-nitrobenzoic (ratio of 1 : 1, diethyl ether) acids provided diphenylbismuth carboxylates [11, 12]. The reaction of triphenylbismuth with trifluoroacetic acid (ratio of 1 : 1 or 1 : 2, diethyl ether, 2.5–12 h) led to the successive substitution of two phenyl groups [13].

By the present time more than 90 bismuth tricarboxylates have been characterized by means of X-ray diffraction analysis, whereas phenylbismuth dicarboxylates and diphenylbismuth carboxylates have been significantly less investigated (only 15 and 6 representatives, respectively) [14].

Investigations of methods of the synthesis of bismuth(III) carboxylates are not restricted only to the variation of the carboxylate ligands and determination of their structure-forming role in the complexes formation, but they also include the detailed investigation of

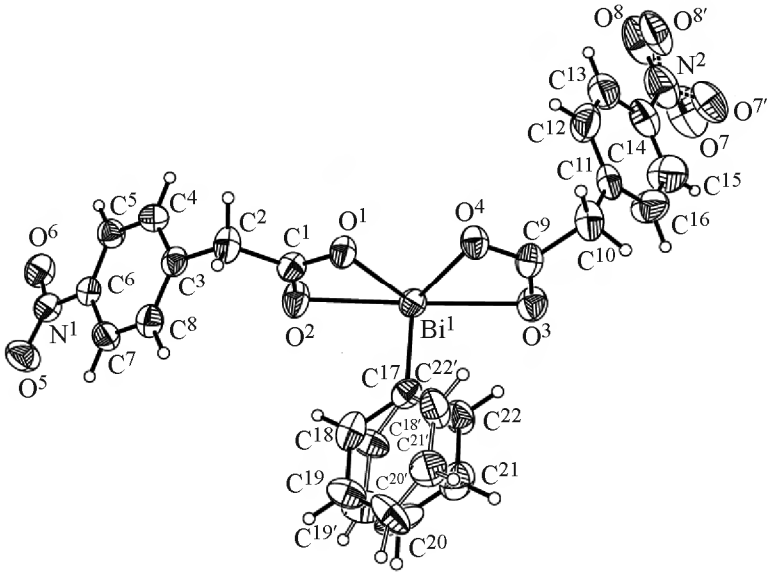

Fig. 1. General view of the molecule of complex **I**.

the influence of solvent nature and molar ratio of the reagents on the substitution of the phenyl groups in triphenylbismuth by carboxylic acids.

We have studied reactions of triphenylbismuth with 4-nitrophenylacetic and 2-nitrobenzoic acids in toluene at 90°C. Thus, at equimolar ratio of the reagents, phenylbismuth bis(4-nitrophenyl)acetate **I** and phenylbismuth bis(2-nitrobenzoate) were formed in 49 and 46% yield, respectively. The minor products of the reactions were diphenylbismuth 4-nitrophenylacetate (27%) and diphenylbismuth 2-nitrobenzoate **II** (16%).

The structure of compounds **I** and **II** was established by XRD method. Bismuth atom in compound **I** occurred to have distorted octahedral coordination with the apically located phenyl ligand and the lone electron pair (Fig. 1). The phenyl group was virtually perpendicular to the plane of one of the equatorial carboxylate ligands [$C^{17}Bi^1O^1$ 90.4(2)°, $C^{17}Bi^1O^2$ 89.6(2)°, $O^2Bi^1O^3$ 175.0(2)°].

The calculation of the planes passing through the atoms of metal-containing rings BiO_2C in the structure of complex **I** showed that the maximal deviation of the atoms from the mean-square plane (0.071 Å) was observed in metal-containing ring $Bi^1O^3O^4C^9$. The dihedral angle between planes $O^3Bi^1O^4$ and $O^3C^9O^4$ was 12.71°. For the second ligand these values (0.007 Å and 1.22°) evidenced a practically flat structure of the metal-containing ring $Bi^1O^1O^2C^1$.

One of the oxygen atoms of each carboxylate ligand coordinated to bismuth atom of the neighboring molecule [Bi^1O^{1A} 3.327(5) Å, Bi^1O^{4A} 3.019(5) Å] thus combining the molecules of phenylbismuth bis(4-nitrophenyl)acetate into chains (Fig. 2). The layers were formed through the contacts of oxygen atom of the nitro group of one carboxylate ligand with bismuth atom of the neighboring chain (Bi^1-O^{6B} 3.248 Å) that was accompanied by the reduction of the value of the torsion angle $O^2C^1C^2C^3$ (7.63°) compared to the value of angle $O^3C^9C^{10}C^{11}$ (69.99°) of the other carboxylate ligand, whose nitro group was not involved in the interaction with a bismuth atom. The intramolecular interaction Bi^1-O^{6B} led to lengthening of the N^1-O^6 bond [1.225(9) Å] compared to the other N–O distances [1.207(9), 1.217(10), 1.219(10) Å]. The nitrogen atoms of the nitro groups were found to be sp^2-hybridizied that was proven by the angles values [$O^6N^1C^6$ 116.5(7)°, $O^5N^1C^6$ 117.8(8)°, $O^5N^1O^6$ 125.5(8)°, $O^7N^2O^8$ 116.0(3)°, $O^7N^2C^{14}$ 121.0(2)°, $O^8N^2C^{14}$121(3)°].

Bismuth atom in the crystal of compound **II** had a trigonal-bipyramidal coordination with apically located oxygen atoms of 2-nitrobenzoate substituents (Fig 3). The phenyl ligands and the lone pair occupied the equatorial plane. The values of angles $O^3Bi^1O^{4A}$ [164.06(13)°] and $C^8Bi^1C^{14}$ [98.38(19)°] evidenced significant distortion of the trigonal-bipyramidal coordination of the bismuth atom. The molecules of the layer formed chains $[-Bi-O-Bi-O-]_n$ along 0*b* axis through the interactions of bismuth atoms with oxygen atoms Bi^1-O^{4A} 2.308(3), Bi^1-O^3 2.578(3), and Bi^1-O^{3A} 3.087(4) Å.

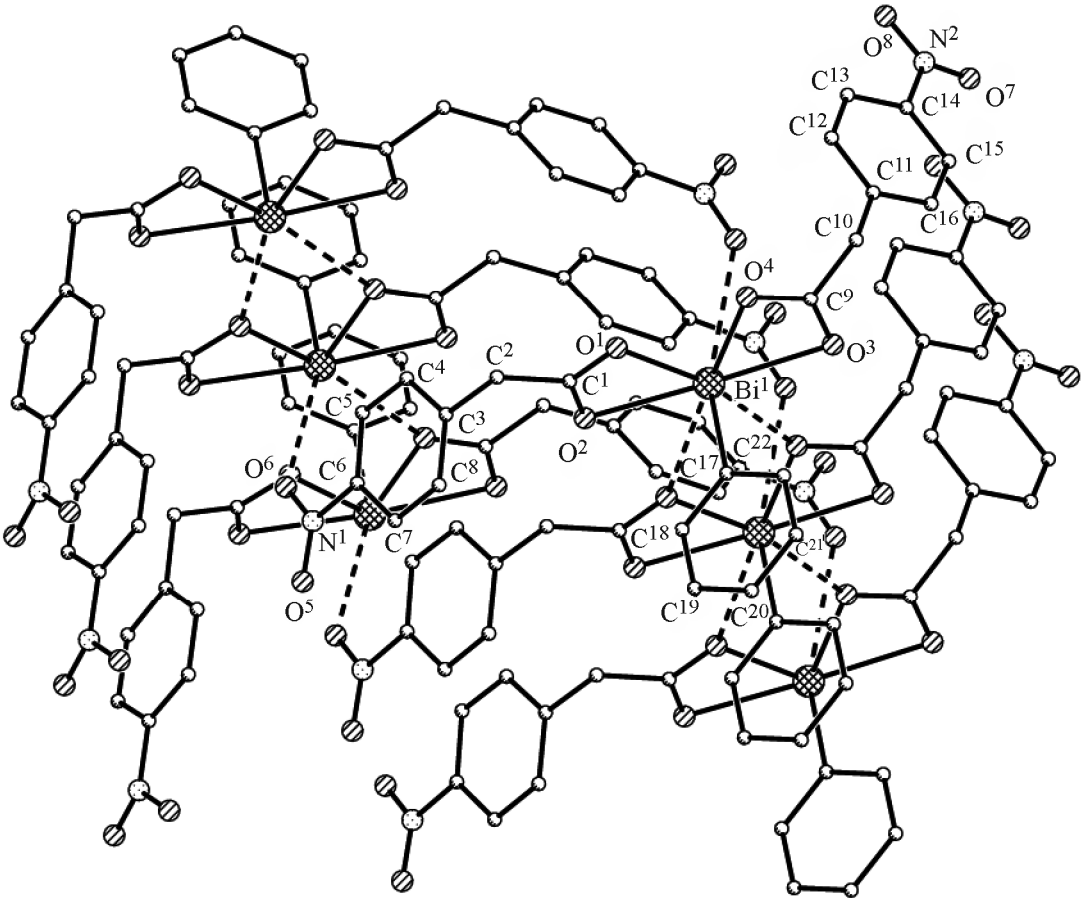

Fig. 2. Crystal packing of molecules in a crystal of complex **I** (hydrogen and disordered atoms are omitted).

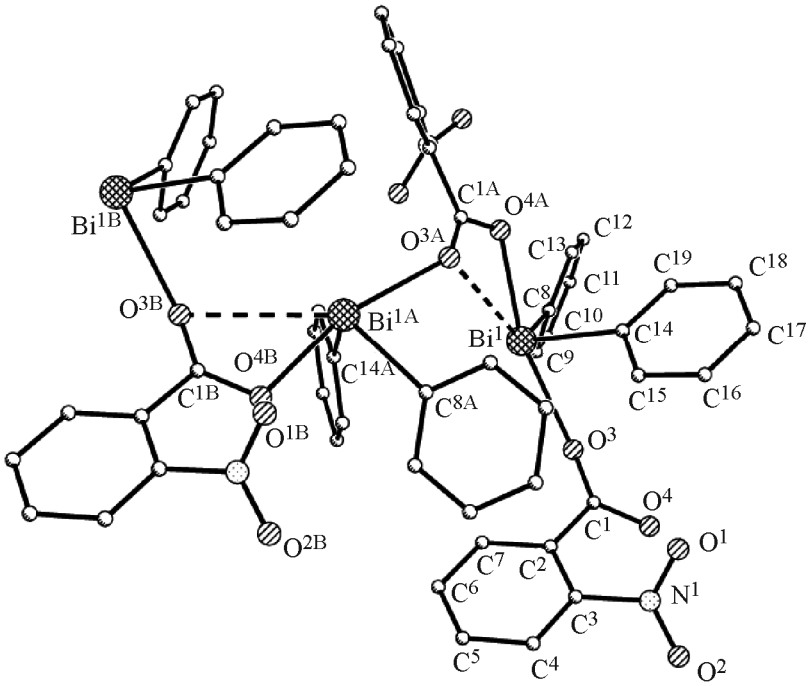

Fig. 3. A fragment of packing (chain $[-Bi-O-Bi-O-]_n$) in the crystal of compound **II**.

Crystallographic data of complexes **I** and **II**

Parameter	**I**	**II**
Empirical formula	$C_{22}H_{17}N_2O_8Bi_1$	$C_{19}H_{14}N_1O_4Bi_1$
Crystal system	Orthorhombic	Monoclinic
M	646.36	529.29
Space group	$P2_12_12_1$	$P2_1/n$
a, Å *b*, Å *c*, Å β, deg	4.7773(5) 17.6366(17) 25.633(3)	13.6819(18) 9.2690(12) 13.9597(19) 99.804(3)
V, Å^3	2159.7(4)	1744.5(4)
Z	4	4
T, K	295(2)	295(2)
d_{calc}, g/cm^3	1.988	2.015
F(000)	1240	1000
Range of θ	$2.44 \le \theta \le 25.99$	$1.93 \le \theta \le 26.00$
Range of indexes measurement	$-5 \le h \le 5$	$-16 \le h \le 16$
	$-21 \le k \le 21$	$-11 \le k \le 11$
	$-31 \le l \le 31$	$-17 \le l \le 17$
Reflections measured Independent reflections	19259 4228	15102 3432
R_{int}	0.0559	0.0414
Number of refined parameters	350	226
$\Delta\rho_{max}/\rho_{min}$, *e*/Å^3	2.132/–0.591	2.159/–0.560
GOOF	1.012	1.009
R-Factors [$I > 2\sigma(I)$]		
R	0.0344	0.0326
R_w	0.0755	0.0826

The lengths of bonds Bi–C [2.212(7) (**I**) and 2.238, 2.245 Å (**II**)] were comparable with the distance Bi–C in the structurally characterized phenylbismuth dicarboxylates (2.222–2.263 Å) and diphenylbismuth carboxylates (2.187–2.250 Å) [14].

In tridentate nitrophenylacetate and nitrobenzoate ligands playing a role of chelates, the distances Bi–O are nonequivalent [Bi^1–O^1 2.327(5), $Bi^1\cdots O^2$ 2.504(5), Bi^1–O^4 2.362(5), $Bi^1\cdots O^3$ 2.546(6) Å (**I**), and Bi^1–O^{4A} 2.308(3), $Bi^{1A}\cdots O^{3A}$ 2.578(3) Å (**II**), the sum of the covalent and Van der Waals radii of the indicated atoms being 2.31 and 3.9 Å] [15]. A ratio of BiO=C distance to the length of Bi–O bond was suggested as a measure of bidentate character of the carboxylate ligand (in a symmetrical bidentate carboxylate ligand this ratio was 1) [16]. In compounds **I** and **II** this value was 1.08 and 1.12 Å. In the known phenylbismuth dicarboxylates the ratio varied within the ranges of 1.05–1.16 and 1.00–1.12. Intramolecular contacts BiO=C in compounds **I** and **II** govern the redistribution of the electron density in carboxylic groups that somehow aligned length of bonds C^1–O^1, C^1–O^2, C^9–O^4, C^9–O^3 and C^1–O^3, C^1–O^4 [1.269(9), 1.233(9), 1.282(9), 1.209(10), and 1.268(6), 1.224(6) Å] compared to the corresponding bonds length in

molecules of 4-nitrophenylacetic and 2-nitrobenzoic acids [1.292(4), 1.235(5) and 1.295(9), 1.233(9) Å] [17, 18].

EXPERIMENTAL

IR spectra were recorded on a FSM 1201 Fourier spectrometer within the interval of 400–4000 cm^{-1} from KBr pellets. X-Ray diffraction studies of the monocrystals were done on a Bruker SMART CCD diffractometer at 295(2) K (λMoK_α-irradiation, $2\theta_{max}$ = 52°). The obtained independent reflections after averaging the equivalent reflections were used for solving and refinement of the structures. The extinction was accounted with the help of SADABS program [19]. The structures were solved by the direct method; all non-hydrogen atoms were located by the difference syntheses of electron density and refined with respect to F^2_{hkl} in the anisotropic approximation; all hydrogen atoms were placed into the geometrically calculated positions and refined by a *rider* model. The calculations were performed using SHELXTL program package [20].

The main crystallographic characteristics of complexes **I** and **II**, experimental data, and parameters of the structures refinement are given in the table. The XRD data were deposited in the Cambridge Crystallographic Data Centre [CCDC 969922 (**I**), 969920 (**II**)].

Phenylbismuth bis(4-nitrophenyl)acetate (I). A mixture of triphenylbismuth [7] (0.50 g, 1.136 mmol) and 4-nitrophenylacetic acid (0.20 g, 1.136 mmol) in 50 mL of toluene was heated for 4 h in a sealed ampule at 90°C. The solvent was decanted; the solid residue was washed with diethyl ether (2 × 15 mL), and filtered off. Yield 0.35 g (49%), colorless needle-like crystals, mp 168°C. IR spectrum, ν, cm^{-1}: 1599 (C=O), 1510 (Ph), 1280 (C–O), 1543 (NO_2). Found, %: C 41.03; H 2.43; N 4.12. $C_{22}H_{17}N_2O_8Bi_1$. Calculated, %: C 40.84; H 2.63; N 4.33.

Diphenylbismuth 4-(nitrophenyl)acetate. Yield 0.16 g (27%), pale brown crystals, mp 148°C. IR spectrum, ν, cm^{-1}: 1601 (C=O), 1512 (Ph), 1278 (C–O), 1548 (NO_2). Found, %: C 44.37; H 2.73; N 2.39. $C_{20}H_{16}N_1O_4Bi_1$. Calculated, %: C 44.17; H 2.94; N 2.58.

Diphenylbismuth 2-nitrobenzoate (II) was obtained similarly from triphenylbismuth (1.00 g, 2.27 mmol) and 2-nitrobenzoic acid (0.38 g, 2.27 mmol). As the reaction products compound **II** (0.19 g, 16%) and phenylbismuth bis(2-nitrobenzoate) (0.64 g, 46%) were isolated; their physicochemical data and parameters of the IR spectra were identical to those described earlier [10, 12].

Diphenylbismuth 4-(nitrophenyl)acetate. A mixture of triphenylbismuth (0.50 g, 1.136 mmol) and 4-nitrophenylacetic acid (0.20 g, 1.136 mmol) in 50 mL of diethyl ether was kept in a sealed ampule at room temperature for 5 days. The solvent was decanted; the solid residue was washed with diethyl ether (2 × 15 mL). Yield 0.31 g (52%); the physicochemical data and parameters of the IR spectra of the compound were identical to those obtained for the compound prepared from triphenylbismuth and 4-nitrophenylacetic acid in toluene at 90°C.

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