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Synthesis and Structure of Bismuth Complexes $[(2\text{-MeO})(5\text{-Cl})C_6H_3]_3Bi$, $[(2\text{-MeO})(5\text{-Cl})C_6H_3]_3Bi[OC(O)CF_2Br]_2$, and $[(2\text{-MeO})(5\text{-Br})C_6H_3]_3Bi[OC(O)C_6HF_4\text{-}2,3,4,5]_2$

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Abstract—In the crystal of $[(2\text{-MeO})(5\text{-Cl})C_6H_3]_3Bi$ (**I**), obtained from bismuth trichloride and 2-methoxy-5-chlorophenyllithium in ether, bismuth atoms have a trigonal ligand environment. The coordination number of the central atom is 6 (3 + 3), with allowance made for the coordination of the MeO oxygen atom to the metal (the Bi···OMe intramolecular distances are 3.014(6), 3.088(6), and 3.168(6) Å). Treatment of a mixture of **I** and bromodifluoroacetic acid, or $[(2\text{-MeO})(5\text{-Br})C_6H_3]_3Bi$ and 2,3,4,5-tetrafluorobenzoic acid in ether with *tert*-butyl hydroperoxide results in the formation of trigonal bipyramidal triarylbismuth dicarboxylates $[(2\text{-MeO})(5\text{-Cl})C_6H_3]_3Bi[OC(O)CF_2Br]_2$ (**II**) and $[(2\text{-MeO})(5\text{-Br})C_6H_3]_3Bi[OC(O)C_6HF_4\text{-}2,3,4,5]_2$ (**III**), respectively, with carboxyl ligands in the apical positions. In the crystals of **II** and **III**, the metal atom is additionally coordinated to the oxygen atoms of the O=C and MeO groups (3.05(16), 3.30(16), and 3.153(5)–3.117(5) Å for **II** and 3.004(7), 3.230(7), and 3.159(7)–3.199(7) Å for **III**). The structures of **I**–**III** were studied by X-ray diffraction (CIF file CCDC nos. 2044006 (**I**), 2044005 (**II**), and 2048153 (**III**)).

Keywords: tris(2-methoxy-5-chlorophenyl)bismuth bis(bromodifluoroacetate), tris(2-methoxy-5-bromophenyl)bismuth bis(2,3,4,5-tetrafluorobenzoate), synthesis, structure, X-ray diffraction

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INTRODUCTION

Until recently, phenyl and, to a lesser extent, *p*-tolyl derivatives were the most studied aryl derivatives of bismuth. Owing to the presence of vacant *d* orbitals, bismuth atoms can form additional coordination bonds with ligands containing sterically accessible atoms with lone electron pairs. This increases the coordination number (C.N.) of the metal and often affects the reactivity of compounds. In some known bismuth aryl derivatives, phenyl substituents contain potential coordination sites such as nitrogen [1–10], oxygen [10–13], phosphorus [14, 15], boron [16], or sulfur atoms [10, 17, 18]. It is known that triarylbismuth dicarboxylates have antileishmanial action [19–22] and possess high photochemical activity [23]; therefore, the synthesis and study of properties of triarylbismuth dicarboxylates with potential coordination sites in aryl ligands are relevant tasks.

In this communication, we report the first synthesis of the complex $[(2\text{-MeO})(5\text{-Cl})C_6H_3]_3Bi$ (**I**) and study of its reaction with bromodifluoroacetic acid in the presence of *tert*-butyl hydroperoxide, resulting in the formation of $[(2\text{-MeO})(5\text{-Cl})C_6H_3]_3Bi[OC(O)CF_2Br]_2$ (**II**). The complex $[(2\text{-MeO})(5\text{-Br})C_6H_3]_3Bi[OC(O)C_6HF_4\text{-}2,3,4,5]_2$ (**III**) was synthesized in a similar way and characterized, after recrystallization from benzene, as a benzene solvate (**III**·1/2PhH). Structural features of the resulting compounds were established.

EXPERIMENTAL

Commercial *para*-chloroanisole, bromodifluoroacetic acid, and 2,3,4,5-tetrafluorobenzoic acid (Alfa Aesar) were used. Tris(2-methoxy-5-bromophenyl)bismuth was prepared by the same procedure as complex **I**. Prior to the synthesis, reagent grade benzene and octane were dried over calcium chloride, and diethyl ether was dried over sodium.

Synthesis of tris(2-methoxy-5-chlorophenyl)bismuth (I). A solution of 5-chloro-2-methoxyphenyllithium in diethyl ether (150 mL), prepared by metallation of *para*-chloroanisole (7.00 g) with phenyllithium, was added to a mixture of bismuth trichloride (5.05 g, 16.0 mmol) and diethyl ether (100 mL). The mixture was stirred and kept for 18 h at 20°C. Water (2 mL) was added to the reaction mixture, and the

ether solution was filtered and concentrated. The yield of the colorless crystals of **I** was 7.08 g (70%). T_m = 189°C.

IR (ν, cm^{-1}): 2955, 2934, 2901, 1564, 1455, 1431, 1377, 1288, 1280, 1259, 1231, 1177, 1138, 1097, 1041, 883, 804, 797, 665, 638, 538, 434.

For $C_{21}H_{18}O_3Cl_3Bi$		
Anal calcd., %	C, 39.75	H, 2.84
Found, %	C, 39.60	H, 2.91

Synthesis of tris(2-methoxy-5-chlorophenyl)bismuth bis(bromodifluoroacetate) (II). A 70% aqueous solution of *tert*-butyl hydroperoxide (0.02 g) was added to a mixture of complex **I** (0.10 g, 0.16 mmol) and bromodifluoroacetic acid (0.055 g, 0.32 mmol) in ether (20 mL). Evaporation of the solvent (12 h) gave colorless crystals of **II**, which were isolated from the reaction mixture, washed with diethyl ether (1 mL), and dried in air. The yield of **II** was 77%. T_m = 105°C.

IR (ν, cm^{-1}): 3088, 3005, 2945, 2843, 1714, 1689, 1583, 1558, 1473, 1440, 1386, 1352, 1280, 1267, 1249, 1166, 1149, 1139, 1105, 1033, 1004, 933, 871, 815, 705, 669, 640, 601, 542, 530, 426.

For $C_{25}H_{18}O_7F_4Cl_3Br_2Bi$		
Anal. calcd., %	C, 30.58	H, 1.83
Found, %	C, 30.29	H, 1.89

Synthesis of tris(2-methoxy-5-bromophenyl)bismuth bis(2,3,4,5-tetrafluorobenzoate) (III) was performed similarly to the synthesis of complex **II**, but using $[(2\text{-MeO})(5\text{-Br})C_6H_3]_3Bi$, prepared by a reported procedure [13], in place of complex **I**. The yield of **III** was 88%. Recrystallization of **III** from benzene gave colorless crystals of **III**·1/2PhH, suitable for X-ray diffraction study. T_m = 134°C.

IR (ν, cm^{-1}): 3068, 3039, 3005, 2991, 2953, 2931, 2900, 2833, 1722, 1624, 1558, 1525, 1456, 1433, 1373, 1309, 1282, 1259, 1232, 1176, 1143, 1136, 1085, 1037, 1014, 914, 896, 883, 796, 765, 713, 694, 655, 613, 532, 516, 433.

For $C_{38}H_{23}O_7F_8Br_3Bi$		
Anal. calcd., %	C, 38.25	H, 1.93
Found, %	C, 38.12	H, 2.06

IR spectra of compounds **I**–**III** were measured on a Shimadzu IR Affinity-1S IR spectrometer in the 4000–400 cm^{-1} range (KBr pellets).

X-ray diffraction study was carried out on a D8 QUEST Bruker four-circle automated diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator) at 293 K. The data collection and editing, refinement of unit cell parameters, application of absorption corrections, and structure solution and refinement were carried out using known software [24–26]. The structures were solved by direct methods and refined by the least-squares calculations in the anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were determined geometrically by the riding model. The crystallographic data and structure refinement details are summarized in Table 1.

The full tables of atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (no. 2044006 (**I**), no. 2044005 (**II**), and no. 2048153 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/structures).

RESULTS AND DISCUSSION

Tris(2-methoxy-5-chlorophenyl)bismuth (**I**) was synthesized from 2-methoxy-5-chlorophenyllithium and bismuth trichloride in diethyl ether:

$$3[(2\text{-MeO})(5\text{-Cl})C_6H_3]Li + BiCl_3 \rightarrow [(2\text{-MeO})(5\text{-Cl})C_6H_3]_3Bi + 3LiCl. \quad (I)$$

Tris(2-methoxy-5-chlorophenyl)bismuth bis(bromodifluoroacetate) (**II**) was prepared in 77% yield from triarylbismuth and bromodifluoroacetic acid in the presence of *tert*-butyl hydroperoxide in diethyl ether

$$\mathbf{I} + 2HOC(O)R + t\text{-BuOOH} \rightarrow [(2\text{-MeO})(5\text{-Cl})C_6H_3]_3Bi[OC(O)R]_2 + t\text{-BuOH} + H_2O, \quad R = CF_2Br. \quad (II)$$

Tris(2-methoxy-5-bromophenyl)bismuth bis(2,3,4,5-tetrafluorobenzoate) (**III**) was prepared in a similar way from tris(2-methoxy-5-bromophenyl)bismuth [13].

$$[(2\text{-MeO})(5\text{-Br})C_6H_3]_3Bi + 2HOC(O)C_6HF_4\text{-}2,3,4,5 + t\text{-BuOOH} \rightarrow [(2\text{-MeO})(5\text{-Br})C_6H_3]_3Bi[OC(O)C_6HF_4\text{-}2,3,4,5]_2 + t\text{-BuOH} + H_2O. \quad (III)$$

The IR spectra of compounds **I**–**III** exhibit intense bands at 1230–1281 (O–C), 1458–1474 (Ar), 2934–2945 (H–C_{Alk}), 2843–3088 cm^{-1} (H–C). The intense absorption bands at 1690 (**II**) and 1558 cm^{-1} (**III**) attest to the presence of carbonyl groups in complexes **II** and **III**.

Table 1. Crystallographic data and X-ray experiment and structure refinement details for **I**–**III**

Parameter	**I**	**II**	**III**
M	633.68	981.54	1192.27
System	Triclinic	Triclinic	Triclinic
T, K	293.15	293.15	293.15
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	8.715(9)	10.067(6)	12.353(6)
b, Å	9.055(9)	11.968(7)	13.785(9)
c, Å	14.820(12)	15.463(14)	13.807(7)
α, deg	95.20(4)	103.11(2)	103.44(3)
β, deg	103.39(4)	102.07(2)	97.18(2)
γ, deg	92.05(6)	109.886(17)	114.41(3)
V, Å^3	1131.1(18)	1621(2)	2016(2)
Z	2	2	2
ρ(calcd.), g/cm^3	1.861	2.011	1.964
μ, mm^{-1}	8.166	8.214	7.428
F(000)	604.0	928.0	1134.0
Crystal size, mm	0.35 × 0.31 × 0.13	0.27 × 0.15 × 0.13	0.32 × 0.14 × 0.11
2θ, deg	5.68–55.82	6.06–54.56	6.116–56.026
Ranges of reflection indices	$-11 \le h \le 11$, $-11 \le k \le 11$, $-19 \le l \le 19$	$-12 \le h \le 12$, $-15 \le k \le 15$, $-19 \le l \le 19$	$-16 \le h \le 16$, $-17 \le k \le 18$, $-18 \le l \le 18$
Total number of reflections	38014	37025	61975
Number of unique reflections (R_{int})	5390 (0.0479)	7188 (0.0410)	9593 (0.0689)
Number of reflections with $I > 2\sigma(I)$	4946	6383	7800
Number of refined parameters	256	382	557
GOOF	1.043	1.047	1.035
R factors on $F^2 > 2\sigma(F^2)$	$R_1 = 0.0278$, $wR_2 = 0.0699$	$R_1 = 0.0311$, $wR_2 = 0.0773$	$R_1 = 0.0453$, $wR_2 = 0.1120$
R factors for all reflections	$R_1 = 0.0316$, $wR_2 = 0.0715$	$R_1 = 0.0380$, $wR_2 = 0.0804$	$R_1 = 0.0637$, $wR_2 = 0.1215$
Residual electron density (max/min), e/Å^3	1.48/–1.85	0.98/–1.92	1.82/–1.47

According to X-ray diffraction data, the molecule of **I** has a trigonal bipyramidal geometry (Fig. 1).

The Bi–C bond lengths (2.253(5), 2.259(4), and 2.262(4) Å) are close to the sum of the covalent radii of these atoms (2.36 Å [27]). The oxygen atoms of the MeO groups are coordinated to the bismuth atom (the intramolecular Bi···OMe distances in **I** are 3.014(6), 3.088(6), and 3.168(6) Å). The CBiC angles and intramolecular Bi···O distances are 91.40(16)°, 92.60(15)°, 93.19(15)° and 3.014(6), 3.088(6), 3.168(6) Å, respectively, which is comparable with analogous angles and distances for tris(2-methoxy-5-bromophenyl)bismuth (90.6(4)°–93.9(5)° and 3.007(15)–3.136(19) Å) [13]). The intramolecular contacts present in **I** account for the decrease in the CBiC bond angles in comparison with those in triphenylbismuth (92.25°–94.37° [28]), in which there are no such contacts.

The bismuth atom in **II** and **III** has a distorted trigonal bipyramidal geometry with carboxylate ligands being in axial positions (Figs 2, 3). The fluorine atoms of compound **III**, located in the *ortho*-position of the benzene ring of the carboxylate ligand, are disordered over two positions. The refined occupancy ratio of the disordered positions is 0.56/0.44. The benzene solvate molecule in **III** is disordered over four positions with the carbon occupancy of 0.25.

The sums of bond angles in the equatorial plane are 360° for **II** and 359.8° for **III**; the OBiC angles some-

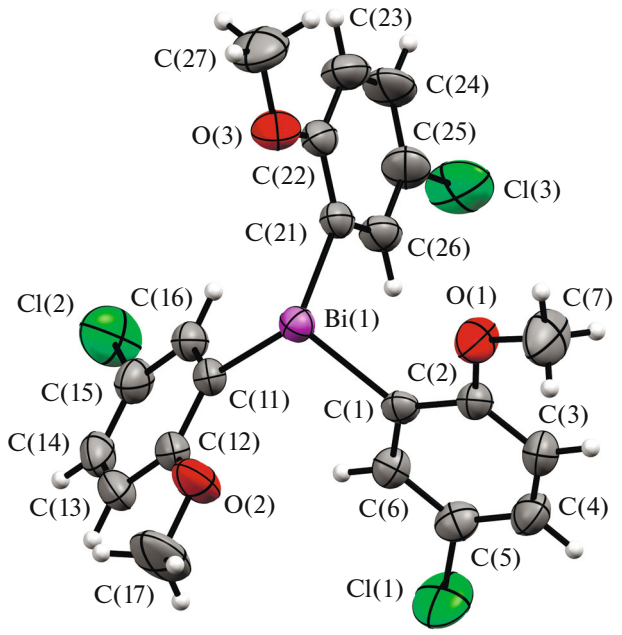

Fig. 1. General view of the molecule of **I**.

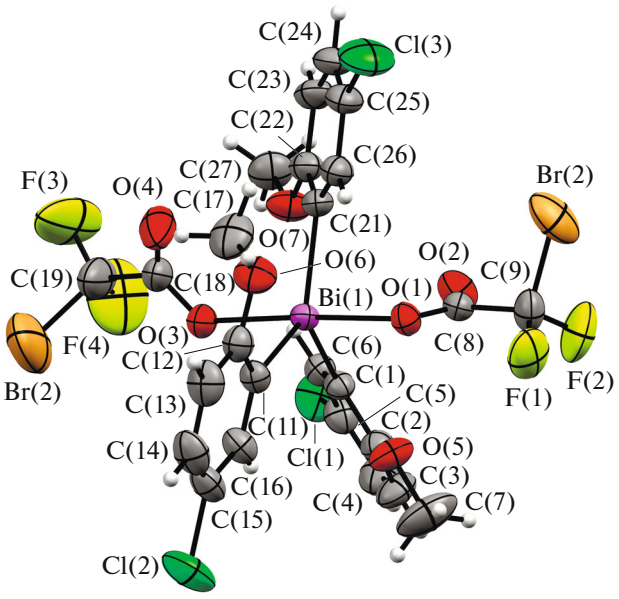

Fig. 2. General view of the molecule of **II**.

what deviate from the theoretical value (81.4(2)°–98.08(16)°). The axial OBiO angles (175.53(12)° and 175.41(17)°) differ from the ideal value of 180°. The Bi–C bond lengths are similar: 2.195(5)–2.204(4) Å in **II** and 2.199(6)–2.201(7) Å in **III**, while the Bi–O distances (2.264(4), 2.315(3) Å in **II** and 2.252(5), 2.295(5) Å in **III**) are comparable with the covalent Bi–O bond lengths (2.32 Å [27]). In triarylbismuth dicarboxylates **II** and **III**, there are intramolecular interactions of the Bi atom with the potential coordination sites of the ligands, that is, oxygen atoms of the methoxy groups. The Bi···OMe distances in **II** and **III** are 3.153(5)–3.117(5) and 3.122(7)–3.199(7) Å, i.e., they are comparable with analogous values for **I**. In triarylbismuth dicarboxylates, there are also intramolecular interactions between the metal atoms and the carbonyl oxygen atoms, with the Bi···O=C distances being 3.05(16), 3.30(16) Å (**II**) and 3.004(7), 3.230(7) Å (**III**), i.e., they are much shorter than the sum of the van der Waals radii of Bi and O atoms (3.9 Å) [27]. Note that similar contacts in tris(2-methoxy-5-bromophenyl)bismuth bis(bromodifluoroacetate), bis(trichloroacetate), and bis(trifluoroacetate) are 3.109–3.566, 3.146, 3.163 and 3.067, 3.146 Å long [13, 28]; therefore, it can be considered that the C.N. of the central atom has increased to 10 (5 + 5).

It is known that carboxylate ligands in structurally characterized triarylbismuth dicarboxylates are usually arranged in such a way that the Bi···O(=C) intramolecular contacts are formed within one equatorial angle, which can increase to 152.9°, while the other two equatorial angles decrease [29, 30]. However, in compounds **II** and **III**, the carbonyl oxygen atoms are

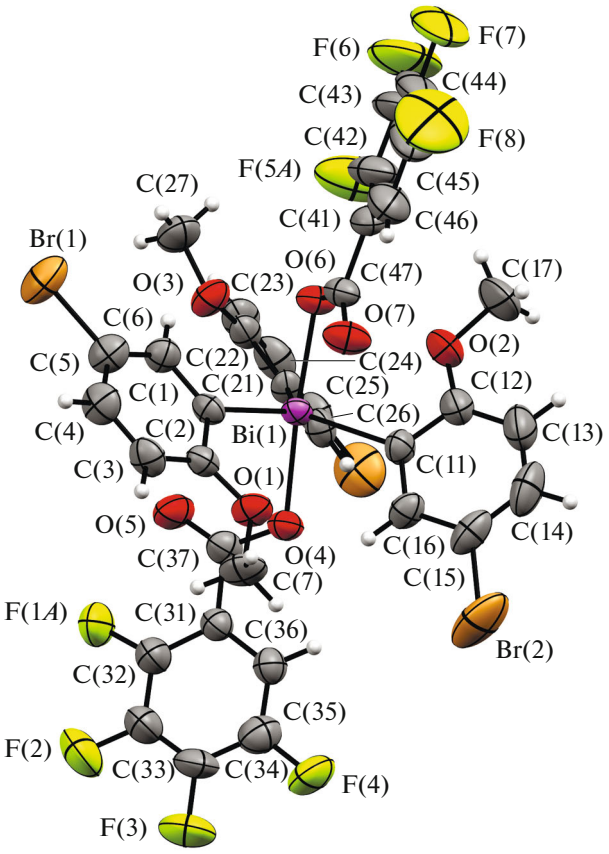

Fig. 3. General view of the molecule of **III** (disordered fluorine atoms and benzene solvate molecule are not shown).

located in front of different equatorial angles (111.55(18)°, 124.34(18)°, 124.11(18)° and 114.3(2)°, 121.9(2)°, 123.6(3)°).

Thus, in compound **I**, the presence of 2-methoxy-5-chlorophenyl ligands containing oxygen atoms with lone pairs at the bismuth atom gives rise to additional non-bonded intramolecular interactions involving the bismuth atom; these contacts also exist in dicarboxylates **II** and **III**. The introduction of electron-withdrawing groups into carboxylate ligands does not noticeably affect the Bi–C bond lengths or the axial angle in the triarylbismuth dicarboxylate molecule. The major difference of the structures of **II** and **III** from other triarylbismuth dicarboxylates is the decrease in the intramolecular Bi···O=C contact, caused by the presence of electron-withdrawing substituents ($CBrF_2$ and C_6HF_4) in the R radicals of the carboxylate ligands, and increase in the C.N. of the central atom to ten (5 + 5).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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