Russian Journal of Coordination Chemistry, Vol. 29, No. 12, 2003, pp. 838–844. Translated from Koordinatsionnaya Khimiya, Vol. 29, No. 12, 2003, pp. 902–908.

Tetranuclear Bismuth Complex $Bi_4(O)_2(O_2CC_6H_2F_3\text{-}3,4,5,)_8 \cdot 2\eta^6\text{-}C_6H_5Me$: Synthesis and Structure

V. V. Sharutin*, I. V. Egorova*, O. K. Sharutina*, T. K. Ivanenko*, N. Yu. Adonin, V. F. Starichenko**, M. A. Pushilin***, and A. V. Gerasimenko*****

**Blagoveshchensk State Pedagogical University, ul. Lenina 104, Blagoveshchensk, 675000 Russia*

***Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

****Institute of Chemistry, Far East Division, Russian Academy of Sciences, pr. Stoletiya Vladivostoka 109, Vladivostok, 690022 Russia*

Received December 9, 2002

Abstract—Tetranuclear organobismuth complex $Bi_4(O)_2(O_2CC_6H_2F_3\text{-}3,4,5)_8 \cdot 2\eta^6\text{-}C_6H_5Me$ with four bismuth atoms joined via the bridging carboxylate ligands and oxygen atoms was studied using X-ray diffraction analysis. The coordination sphere of either of the two terminal bismuth atoms contains the chelate carboxylate ligand and the toluene molecule. For the bridging tricoordinated oxygen atoms, the Bi–O distances are 2.083(2), 2.119(2), and 2.276(2) Å. The average distance between the bismuth atom and the center of toluene molecule is equal to 3.131 Å.

A number of bismuth complexes containing η^6-arene molecules were reported in [1–9]; however, only one polynuclear bismuth compound of this type with bridging oxygen-containing ligand was described in [2], namely, the hexanuclear organobismuth complex. In this compound, the coordination sphere of the bismuth atoms contains, in addition to the η^6-toluene and η^1-tetrahydrofurane, the bridging oxygen atoms and pentafluorophenolate ligands (two terminal and ten bridging) [2]. The Bi···C_6H_5Me distance (3.073 Å) is noticeably shorter that the sum of the van der Waals radii of bismuth and oxygen.

In this work, the synthesis and X-ray diffraction analysis of tetranuclear organobismuth complex $Bi_4(O)_2(O_2CC_6H_2F_3\text{-}3,4,5)_8 \cdot 2\eta^6\text{-}C_6H_5Me$ (**I**) are described.

RESULTS AND DISCUSSION

Complex **I** was synthesized by reacting triphenylbismuth with 3,4,5-trifluorobenzoic acid (at a molar ratio of 1 : 2) in the presence of air oxygen:

$$4Ph_3Bi + 8C_6H_2F_3\text{-}3,4,5(O)COH + O_2 \xrightarrow{\text{toluene}} Bi_4(O)_2[OC(O)C_6H_2F_3\text{-}3,4,5]_8 \cdot 2C_6H_5Me.$$

It was established that triphenylbismuth is completely dephenylated under these conditions.

According to X-ray diffraction data, centrosymmetrical tetranuclear complex **I** contains two pairs of structurally nonequivalent Bi atoms: two central (Bi(1) and Bi(1)') and two terminal (Bi(2) and Bi(2)') (Fig. 1). The bidentate 3,4,5-trifluorobenzoate ligands perform different structural functions: six of them act as the bridging ligands, while the remaining two ligands behave as chelate ligands.

The central Bi atom is linked to one terminal Bi atom through two bridging carboxylate ligands and the bridging O atom and is bonded to another ligand through the bridging carboxylate ligand and the bridging O atom (Fig. 2). The μ_3-bridging O atom is joined with two central and one terminal Bi atoms, thus closing centrosymmetrical four-membered Bi(1)O(1)Bi(1)'O(1)' ring. The Bi(1)–O(1) and Bi(1)–O(1)' distances in this ring are equal to 2.119(2) and 2.276(2) Å, respectively; the Bi(2)–O(1) bond length is equal to 2.083(2) Å (the sum of the covalent radii of the Bi and O atoms is equal to 2.31 Å [10]).

All the three bridging carboxylate ligands are asymmetrically coordinated to the Bi atoms, the coordination asymmetry being different. The Bi(1)–O(7) and Bi(2)–O(6), Bi(1)–O(9) and Bi(2)–O(8) distances are equal to 2.387(3) and 2.413(3), 2.384(3) and 2.241(3) Å, respectively. The difference between the two bonds of these ligands (Δ) is equal to 0.026 and 0.143 Å, respectively. The Bi(1)–O(4) and Bi(2)'–O(5) distances are equal to 2.308(3) and 2.595(3) Å (Δ = 0.287 Å), i.e. the coordination asymmetry of the Bi atoms in this carboxylate ligand is most pronounced.

The coordination sphere of each terminal bismuth atom contains one chelate carboxylate ligand. The Bi(2)–O(2) and Bi(2)–O(3) distances are equal to 2.349(3) and 2.616(3) Å, respectively. Evidently, the longer distances Bi(2)–O(3), Bi(2)'–O(3)' (2.616(3) Å) and Bi(2)–O(5)', Bi(2)'–O(5) (2.595(3) Å) are due to

1070-3284/03/2912-0838$25.00 © 2003 MAIK "Nauka / Interperiodica"

Table 1. Crystallographic data and details of data collection and refinement for structure **I**

Parameter	Value
Empirical formula	$C_{70}H_{24}Bi_4F_{24}O_{18}$
M	2436.75
Crystal system	Triclinic
T, K	293(2)
Space group	$P\bar{1}$
Unit cell parameters:	
a, Å	11.072(1)
b, Å	13.295(2)
c, Å	14.011(2)
α, deg	76.687(2)
β, deg	74.532(2)
γ, deg	69.281(2)
V, Å^3	1838.1(4)
Z	1
ρ(calcd), g/cm^3	2.201
μ_{Mo}, mm^{-1}	9.675
F(000)	1128
Crystal form (size, mm)	Prism (0.33 × 0.21 × 0.14)
θ, deg	2.98–30.04
Range of reflection indices	$-15 \le h \le 15$, $-17 \le k \le 18$, $-19 \le l \le 19$
Total number of reflections	20216
Independent reflections	10473 (R_{int} = 0.0425)
Reflections with $I > 2\sigma(I)$	5560
Number of refined parameters	511
GOOF	0.762
R-factors for $F^2 > 2\sigma(F^2)$	R_1 = 0.0325, wR_2 = 0.0605
R-factors for all reflections	R_1 = 0.0789, wR_2 = 0.0675
Residual electron density (min/max), *e*/Å^3	–0.785/1.160

Table 2. Coordinates of atoms ($\times 10^4$) and their isotropic equivalent thermal parameters ($\times 10^3$) in structure **I**

Atom	*x*	*y*	*z*	U_{eq}, Å^2	Atom	*x*	*y*	*z*	U_{eq}, Å^2
Bi(1)	10740.9(1)	–504.6(1)	1076.4(1)	39.55(4)	C(13)	8595(5)	4933(4)	–2857(4)	77.5(17)
Bi(2)	7362.7(1)	1645.4(1)	1261.2(1)	43.10(5)	C(14)	9112(5)	5624(4)	–2622(4)	87.4(19)
F(13)	8376(3)	5091(3)	–3801(2)	122.0(13)	C(15)	9319(5)	5489(4)	–1697(5)	86.1(18)
F(14)	9444(3)	6400(2)	–3311(3)	131.8(14)	C(16)	8987(4)	4691(4)	–959(4)	72.0(15)
F(15)	9817(3)	6163(3)	–1481(3)	149.2(14)	C(21)	13574(4)	1219(3)	–736(3)	50.9(11)
F(23)	16739(3)	1215(3)	–2289(2)	117.9(13)	C(22)	14858(4)	837(4)	–1276(3)	62.3(13)
F(24)	15545(3)	3345(2)	–2327(3)	126.9(12)	C(23)	15486(4)	1581(4)	–1785(3)	73.5(16)
F(25)	13066(4)	4088(3)	–1304(3)	141.6(15)	C(24)	14900(5)	2646(4)	–1794(4)	80.9(16)
F(33)	11674(3)	701(2)	5383(2)	100.6(10)	C(25)	13649(5)	3021(4)	–1283(4)	82.0(16)
F(34)	9683(3)	2219(3)	6344(2)	111.5(11)	C(26)	12965(4)	2316(4)	–730(3)	68.2(14)
F(35)	7519(3)	3300(3)	5588(2)	112.5(11)	C(31)	9362(4)	1532(3)	3744(3)	44.6(11)
F(43)	4303(3)	–1801(3)	4781(3)	147.2(17)	C(32)	10474(4)	988(3)	4127(3)	54.5(12)
F(44)	5478(3)	–3943(3)	4797(3)	147.4(15)	C(33)	10572(4)	1238(4)	4998(3)	67.9(14)
F(45)	7853(4)	–4645(3)	3683(4)	170.9(19)	C(34)	9570(5)	1994(4)	5473(3)	67.6(14)
O(1)	9169(2)	733(2)	505(2)	38.8(7)	C(35)	8482(5)	2528(4)	5095(3)	65.2(14)
O(2)	8152(3)	3119(2)	478(2)	59.9(8)	C(36)	8369(4)	2323(3)	4223(3)	56.1(12)
O(3)	7570(2)	2530(2)	–623(2)	52.9(8)	C(41)	7343(4)	–1777(3)	3064(3)	52.7(12)
O(4)	11761(3)	820(2)	423(2)	62.0(9)	C(42)	6101(4)	–1404(4)	3636(3)	66.8(15)
O(5)	13297(2)	–529(2)	–306(2)	60.8(8)	C(43)	5496(5)	–2155(5)	4211(4)	96(2)
O(6)	7416(3)	–15(2)	2420(2)	59.5(9)	C(44)	6098(5)	–3243(5)	4224(4)	95.2(19)
O(7)	9096(2)	–1381(2)	1830(2)	57.2(8)	C(45)	7283(6)	–3575(4)	3673(4)	99(2)
O(8)	8248(3)	1858(2)	2437(2)	59.2(8)	C(46)	7938(4)	–2875(4)	3075(3)	70.9(15)
O(9)	10057(3)	442(2)	2478(2)	60.3(9)	C(51)	4082(3)	2363(3)	2527(3)	170(4)
C(1)	8031(4)	3168(3)	–416(3)	49.3(12)	C(52)	3975(4)	2691(4)	1528(3)	142(3)
C(2)	12830(4)	443(3)	–170(3)	54.8(12)	C(53)	4426(5)	3542(4)	963(3)	161(4)
C(3)	9227(4)	1234(3)	2809(3)	42.9(10)	C(54)	4984(4)	4064(3)	1397(4)	150(3)
C(4)	8016(4)	–1002(3)	2389(3)	51.3(12)	C(55)	5091(4)	3736(4)	2395(4)	147(3)
C(11)	8442(4)	4020(3)	–1179(3)	54.2(13)	C(56)	4640(4)	2886(4)	2960(3)	149(4)
C(12)	8234(4)	4133(3)	–2146(3)	59.1(13)	C(57)	3534(10)	1584(8)	3008(10)	261(7)

Table 3. Bond lengths and angles in structure **I**

Bond	*d*, Å	Bond	*d*, Å
Bi(1)–O(1)	2.119(2)	F(13)–C(13)	1.363(6)
Bi(1)–O(1)'	2.276(2)	F(14)–C(14)	1.324(5)
Bi(1)–O(4)	2.308(3)	F(15)–C(15)	1.328(6)
Bi(1)–O(9)	2.384(3)	F(23)–C(23)	1.348(5)
Bi(1)–O(7)	2.387(3)	F(24)–C(24)	1.341(5)
Bi(1)–O(3)'	2.782(2)	F(25)–C(25)	1.332(5)
Bi(1)–O(5)	2.967(3)	F(33)–C(33)	1.359(5)
Bi(1)–Bi(1)'	3.5791(4)	F(34)–C(34)	1.368(5)
Bi(1)–Bi(2)'	3.7154(4)	F(35)–C(35)	1.352(5)
Bi(1)–Bi(2)	3.8063(4)	F(43)–C(43)	1.332(5)
Bi(2)–O(1)	2.083(2)	F(44)–C(44)	1.341(6)
Bi(2)–O(8)	2.241(3)	F(45)–C(45)	1.336(6)
Bi(2)–O(2)	2.349(3)	O(1)–Bi(1)'	2.276(2)
Bi(2)–O(6)	2.413(3)	O(2)–C(1)	1.279(5)
Bi(2)–O(5)'	2.595(3)	O(3)–C(1)	1.251(5)
Bi(2)–O(3)	2.616(3)	O(4)–C(2)	1.261(4)
Bi(2)–C(1)	2.848(4)	O(5)–C(2)	1.249(5)
Bi(2)–C(54)	3.367(4)	O(5)–Bi(2)'	2.595(3)
Bi(2)–C(55)	3.396(4)	O(6)–C(4)	1.249(5)
Bi(2)–C(53)	3.397(4)	O(7)–C(4)	1.246(4)
Bi(2)–C(56)	3.455(4)	O(8)–C(3)	1.265(4)
Bi(2)–C(52)	3.456(4)	O(9)–C(3)	1.218(4)
C(24)–C(25)	1.352(6)	C(1)–C(11)	1.476(6)
C(25)–C(26)	1.380(6)	C(2)–C(21)	1.500(6)
C(31)–C(32)	1.367(5)	C(3)–C(31)	1.511(5)
C(31)–C(36)	1.370(5)	C(4)–C(41)	1.494(6)
C(32)–C(33)	1.376(6)	C(11)–C(16)	1.366(7)
C(33)–C(34)	1.346(6)	C(11)–C(12)	1.399(6)
C(34)–C(35)	1.340(6)	C(12)–C(13)	1.373(6)
C(35)–C(36)	1.357(6)	C(13)–C(14)	1.376(8)
C(41)–C(46)	1.371(6)	C(14)–C(15)	1.335(8)
C(41)–C(42)	1.375(5)	C(15)–C(16)	1.378(7)
C(42)–C(43)	1.382(7)	C(21)–C(26)	1.375(6)
C(43)–C(44)	1.359(8)	C(21)–C(22)	1.394(5)
C(44)–C(45)	1.311(7)	C(22)–C(23)	1.367(6)
C(45)–C(46)	1.374(7)	C(23)–C(24)	1.331(7)
C(51)–C(57)	1.34(1)		

Table 3. (Contd.)

Angle	ω, deg	Angle	ω, deg
O(1)Bi(1)O(1)'	71.01(9)	O(8)Bi(2)O(3)	128.80(9)
O(1)Bi(1)O(4)	81.18(9)	O(2)Bi(2)O(3)	52.34(9)
O(1)'Bi(1)O(4)	89.78(9)	O(6)Bi(2)O(3)	145.22(9)
O(1)Bi(1)O(9)	85.88(9)	O(5)'Bi(2)O(3)	71.37(9)
O(1)'Bi(1)O(9)	156.11(8)	O(1)Bi(2)C(53)	144.22(9)
O(4)Bi(1)O(9)	80.6(1)	O(8)Bi(2)C(53)	115.0(1)
O(1)Bi(1)O(7)	83.43(9)	O(2)Bi(2)C(53)	82.0(1)
O(1)'Bi(1)O(7)	94.08(9)	O(6)Bi(2)C(53)	120.0(1)
O(4)Bi(1)O(7)	161.95(9)	O(5)'Bi(2)C(53)	84.4(1)
O(9)Bi(1)O(7)	89.0(1)	O(3)Bi(2)C(53)	71.71(8)
O(1)Bi(1)O(3)'	136.54(9)	C(1)Bi(2)C(53)	75.6(1)
O(1)'Bi(1)O(3)'	67.61(8)	O(1)Bi(2)C(56)	167.91(9)
O(4)Bi(1)O(3)'	110.96(8)	O(8)Bi(2)C(56)	76.7(1)
O(9)Bi(1)O(3)'	136.26(8)	O(2)Bi(2)C(56)	100.7(1)
O(7)Bi(1)O(3)'	86.75(8)	O(6)Bi(2)C(56)	86.0(1)
O(1)Bi(1)O(5)	110.43(8)	O(5)'Bi(2)C(56)	109.4(1)
O(1)'Bi(1)O(5)	66.38(8)	O(3)Bi(2)C(56)	118.04(9)
O(4)Bi(1)O(5)	47.69(8)	C(1)Bi(2)C(56)	111.7(1)
O(9)Bi(1)O(5)	118.91(9)	Bi(2)O(1)Bi(1)	129.9(1)
O(7)Bi(1)O(5)	148.80(9)	Bi(2)O(1)Bi(1)'	116.8(1)
O(3)'Bi(1)O(5)	63.74(8)	Bi(1)O(1)Bi(1)'	108.99(9)
Bi(1)'Bi(1)Bi(2)	60.315(6)	Bi(2)'O(5)Bi(1)	83.54(8)
Bi(2)'Bi(1)Bi(2)	123.188(6)	O(3)C(1)O(2)	121.1(4)
O(1)Bi(2)O(8)	93.39(9)	O(3)C(1)C(11)	122.0(4)
O(1)Bi(2)O(2)	83.63(9)	O(2)C(1)C(11)	116.9(4)
O(8)Bi(2)O(2)	77.51(10)	O(5)C(2)O(4)	124.0(4)
O(1)Bi(2)O(6)	85.17(8)	O(5)C(2)C(21)	118.8(3)
O(8)Bi(2)O(6)	78.62(10)	O(4)C(2)C(21)	117.2(4)
O(2)Bi(2)O(6)	152.91(10)	O(9)C(3)O(8)	126.2(4)
O(1)Bi(2)O(5)'	76.63(9)	O(9)C(3)C(31)	118.3(3)
O(8)Bi(2)O(5)'	154.48(9)	O(8)C(3)C(31)	115.5(3)
O(2)Bi(2)O(5)'	123.57(9)	O(7)C(4)O(6)	125.5(4)
O(6)Bi(2)O(5)'	77.19(9)	O(7)C(4)C(41)	118.3(4)
O(1)Bi(2)O(3)	73.56(8)	O(6)C(4)C(41)	116.1(3)

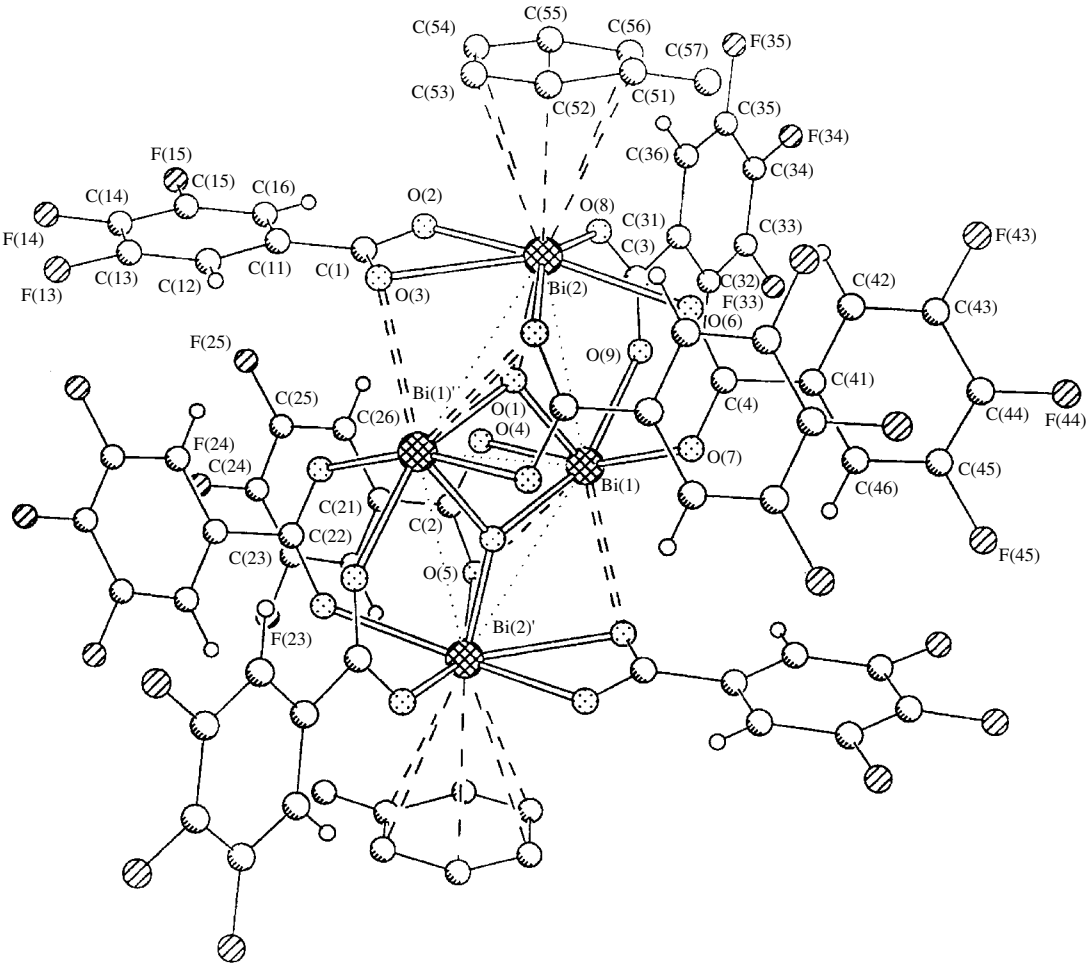

Fig. 1. Molecular structure of complex **I**.

the additional coordination of the O(3), O(5)', and O(3)', O(5) atoms to the Bi(1)' and Bi(1) atoms, respectively (the Bi(1)'–O(3), Bi(1)–O(3)' and Bi(1)–O(5), Bi(1)'–O(5)' distances are equal to 2.782(2) and 2.967(3) Å).

The structure of complex **I** is peculiar in that the distances between its terminal and central bismuth atoms (3.7154(4) and 3.8063(4) Å) are substantially shorter than the doubled van der Waals radius of the bismuth atom (4.8 Å [10]). The distance between the central Bi atoms (Bi(1)'···Bi(1)') is the shortest (3.5791(4) Å). These abnormally short Bi···Bi distances (the twofold covalent radius of the bismuth atom is equal to 3.16 Å [10]) can be explained by a "rigid" structure of the tetranuclear fragment Bi_4O_2, formed due to the presence of the oxygen and carboxylate bridges.

The coordination sphere of the terminal Bi atoms contains the η^6-bonded toluene molecules. The polynuclear bismuth complexes containing the η^6-coordinated arene molecules, in addition to the bridging chlorine, bromine, iodine, and oxygen atoms, also were compared using the Cambridge Structural Database to show that the Bi···η^6-arene distances in these complexes vary within a broad interval (2.243–3.797 Å [1]), while the average value (3.073 Å) is close to that in complex **I** (3.131 Å).

EXPERIMENTAL

Reaction of triphenylbismuth with 3,4,5-trifluorobenzoic acid. A mixture of 0.25 g of triphenylbismuth and 0.20 g of 3,4,5-trifluorobenzoic acid in 20 ml of toluene was kept in a sealed glass tube containing air oxygen at 20°C for 16 h. The crystals formed were filtered off and dried. The yield of complex **I** was 0.33 g (92%), mp 235°C (decomp.).

X-ray diffraction analysis of crystals **I** was carried out on a Bruker SMART CCD 1000 autodiffractometer (graphite monochromator, $\lambda Mo K_\alpha$). The data were collected in sets of 606, 435, and 230 scans at $\varphi = 0°$, 90°, and 180°, respectively; ω scanning with the step of 0.3° and the step counting time of 10 s was used. The crystal–detector distance was equal to 45 mm.

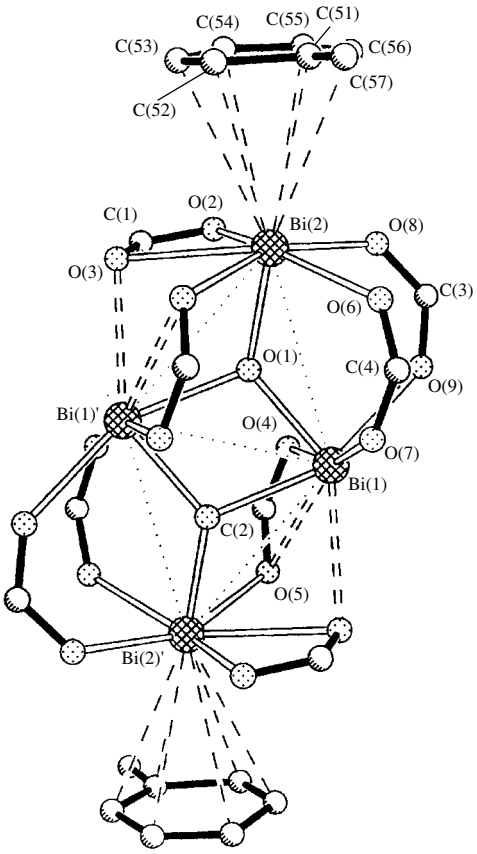

Fig. 2. The structure of organobismuth core in complex **I** (aryl substituents in the carboxylate ligands are not shown).

The structure was solved by the direct methods and refined by the least-squares method in an anisotropic approximation for non-hydrogen atoms. Positions of the hydrogen atoms were calculated geometrically and included in the refinement in the rider model.

Data collection and processing and refinement of the unit cell parameters were carried out using the SMART and SAINT-*Plus* programs [11]. All the calculations were performed using the SHELXTL/PC programs (Version 5.10) [12].

Crystallographic data and the results of refinement of structure **I** are presented in Table 1, coordinates of non-hydrogen atoms are given in Table 2, and bond lengths and angles are listed in Table 3.

REFERENCES

1. *Cambridge Crystallografic Database. Release 2001*, Cambridge.
2. Whitmire, K.H., Hoppe, S., Sydora, O., *et al.*, *Inorg. Chem.*, 2000, vol. 39, no. 1, p. 85.
3. Frank, W., Weber, J., and Fuchs, E., *Angew. Chem., Int. Ed. Engl.*, 1987, vol. 26, no. 1, p. 74.
4. Jones, C.M., Burkart, M.D., and Whitmire, K.H., *Angew. Chem., Int. Ed. Engl.*, 1992, vol. 31, no. 4, p. 451.
5. Jones, C.M., Burkart, M.D., Bachman, R.E., *et al.*, *Inorg. Chem.*, 1993, vol. 32, no. 23, p. 5136.
6. Frank, W., Schneider, J., and Muller-Becker, S., *J. Chem. Soc., Chem. Commun.*, 1993, no. 3, p. 799.
7. Muller-Becker, S., Frank, W., and Schneider, J., *Z. Anorg. Allg. Chem.*, 1993, vol. 619, p. 1073.
8. Frank, W. and Reiland, V., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1999, vol. 54, p. 1626.
9. Frank, W., Reiland, V., and Reiss, G., *Angew. Chem., Int. Ed. Engl.*, 1998, vol. 37, no. 21, p. 2984.
10. Batsanov, S.S., *Zh. Neorg. Khim.*, 1991, vol. 36, no. 12, p. 3015.
11. *Bruker. SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System*, Bruker AXS Inc., Madison, Wisconsin, USA, 1998.
12. *Bruker. SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, Bruker AXS Inc., Madison, Wisconsin, USA, 1998.