Tetranuclear Bismuth Complexes

\[ \text{Bi}_4(O)_2(\text{O}_2\text{C}_6\text{H}_2\text{F}_3\cdot 3,4,5)_8 \cdot 2\text{C}_6\text{H}_6 \]

and \[ \text{Bi}_4(O)_2(\text{O}_2\text{C}_6\text{H}_2\text{F}_3\cdot 3,4,5)_8 \cdot 2\text{C}_6\text{H}_4\text{Me}_2\cdot 1,4: \]

Synthesis and Structures


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Abstract—X-ray diffraction study of tetranuclear organobismuth complexes \( \text{Bi}_4(O)_2(\text{O}_2\text{C}_6\text{H}_2\text{F}_3\cdot 3,4,5)_8 \cdot 2\eta^6\cdot\text{C}_6\text{H}_6 \) and \( \text{Bi}_4(O)_2(\text{O}_2\text{C}_6\text{H}_2\text{F}_3\cdot 3,4,5)_8 \cdot 2(\text{C}_6\text{H}_4\text{Me}_2\cdot 1,4) \) revealed four Bi atoms connected through the bridging carboxylate ligands and the O atoms. The coordination sphere of the terminal Bi atoms includes the chelate carboxylate ligand and the \( \eta^6 \)-arene molecule. The bridging O atoms are tricoordinated, the distances between the terminal Bi atom and the center of benzene molecule (1,4-dimethylbenzene) are 3.024 Å (3.131 Å).

Tetranuclear Bi complexes containing the \( \eta^6 \)-arene molecules and the bridging carboxylate ligands are represented by a single compound \( \text{Bi}_4(O)_2(\text{O}_2\text{C}_6\text{H}_2\text{F}_3\cdot 3,4,5)_8 \cdot 2\eta^6\cdot\text{C}_6\text{H}_6 \) (I) synthesized in [1] from triphenylbismuth and 3,4,5-trifluorobenzoic acid (taken at a molar ratio of 1:2) in the presence of air oxygen (toluene, 12 h, 20°C).

It was found that the reaction between the above reagents in benzene and 1,4-dimethylbenzene results in Bi complexes with the similar structures (II, III):

\[ 4\text{Ph}_3\text{Bi} + 8\text{Ar}(\text{O})\text{COH} + \text{O}_2 \xrightarrow{\text{ArH}} \text{Bi}_4(O)_2[\text{OC}(\text{O})\text{Ar}]_8 \cdot 2\text{ArH}, \]

\[ \text{Ar} = \text{C}_6\text{H}_4\text{F}_3\cdot 3,4,5; \quad \text{Ar'} = \text{C}_6\text{H}_3\text{I} \] (II),

\[ \text{C}_6\text{H}_3\text{Me}_2\cdot 1,4 \] (III).

As follows form X-ray diffraction data, each of complexes II and III, like compound I, contains two pairs of nonequivalent Bi atoms; two central and two peripheral (terminal) Bi atoms (Figs. 1 and 2). The bidentate 3,4,5-trifluorobenzoate ligands perform different structural functions: six ligands act as bridges, while the remaining two ligands act as chelates.

Each central Bi atom is connected to one terminal Bi atom by two bridging carboxylate ligands and the bridging O atom, while it is lined with another terminal Bi atom through a bridging carboxylate ligand and the bridging O atom. As a result, the bridging O atoms connect also two central Bi atoms. Thus, the central fragment of II and III contains four-membered centrosymmetric BiOBO cylic incorporating tricoordinated O atoms.

The distances Bi(1)–O(1) and Bi(1)–O(1)' in II are 2.115(2) Å and 2.275(2) Å, respectively (the analogous distances in I are 2.119(2) Å and 2.276(2) Å; in III, they are 2.124(3) Å and 2.276(3) Å). The distances between the bridging O atom and the terminal Bi atom in I and III are equal to 2.094(2) Å and 2.089(3) Å (in II, this value is 2.083(2) Å) for the sum of the covalent radii of the Bi and O atoms being equal to 2.31 Å [2].

In general, the structures of complexes II and III are similar to that of complex I. As in I, the bridging carboxylate ligands in II and III are nonsymmetrically coordinated to the Bi atoms; the coordination sphere of the terminal Bi atoms contains one chelate carboxylate ligand.

The structures of complexes II and III are peculiar in that the distances between the terminal and central Bi atoms (3.825(1), 3.825(1) and 3.843(1), 3.843(1) Å, respectively) are significantly smaller than the doubled van der Waals radius of the Bi atom (4.8 Å [2]). The shortest distances for both complexes (3.577(4) Å) are observed between the central Bi atoms. Such abnormally short Bi···Bi distances (the doubled covalent radius of the Bi atom being 3.16 Å) can be explained by a "rigid" structure of the Bi\(_2\)O\(_5\) fragment formed due to the presence of the oxygen and carboxylate bridges.

The coordination sphere of the terminal Bi atoms in complexes II and III includes the \( \eta^6 \)-bonded molecules of benzene and 1,4-dimethylbenzene, respectively. The analysis of polynuclear Bi complexes containing the
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The coordination of 

\( \eta^6 \)-coordinated arene molecules, in addition to the bridging Cl, Br, I, and O atoms was performed using the Cambridge Structural Database. It was shown, the Bi···\( \eta^6 \)-arene distances in the above complexes lie in the range of 2.243–3.797 Å [3]. It noteworthy that although the indicated distances vary within a broad range, their average value (3.073 Å) is close to the values discovered in complexes I, II, and III (3.131, 3.024 and 3.131 Å, respectively).

EXPERIMENTAL

**Synthesis of complex II.** A mixture of triphenylbismuth (0.43 g) and 3,4,5-trifluorobenzoic acid (0.35 g) in 20 ml of benzene was stored in a sealed tube containing air oxygen for 16 h at 20°C. The yield of crystals II was 0.60 g (95%); mp 218°C. IR (v, cm\(^{-1}\)): 1540 vs, 1420 s, 1240 w, 1180 w, 1040 s, 990 m.

For C\(_{68}\)H\(_{28}\)Bi\(_4\)O\(_{18}\)F\(_{24}\)

Anal. calcd. (%): C, 33.66; H, 1.16.

Found (%): C, 33.05; H, 1.37.

**Synthesis of complex III.** A mixture of triphenylbismuth (0.43 g) and 3,4,5-trifluorobenzoic acid (0.35 g) in 20 ml of \( n \)-xylene was kept in a sealed tube containing air oxygen for 16 h at 20°C. The yield of the crystalline complex III was 0.60 g (97%); mp 225°C. IR (v, cm\(^{-1}\)): 1630 w, 1580 w, 1530 vs, 1410 s, 1240 s, 1180 w, 1040 vs, 990 w.

For C\(_{72}\)H\(_{36}\)Bi\(_4\)O\(_{18}\)F\(_{24}\)

Anal. calcd. (%): C, 34.84; H, 1.45.

Found (%): C, 34.29; H, 1.98.

IR spectra were recorded on a Hitachi-215 spectrometer (with essential oil mulls between NaCl plates).

**X-ray diffraction analysis** of crystals II and III was performed on a Bruker SMART CCD 1000 automated diffractometer (graphite monochromator, \( \lambda \)MoK\(_\alpha\)). The data for crystal II were collected in sets of 906, 660, and 345 scans at \( \varphi = 0^\circ, 90^\circ \), and 180\(^\circ\), respectively; \( \omega \) scanning at a step of 0.2\(^\circ\) and 20 s per frame. The data for crystal III were collected in sets of