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Synthesis and Structure of a Novel Ladder-Type Organobismuth Compound with Bismuth−Oxygen Interactions

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*Summary: Hydrolysis of 6-tert-butyl-1-p-tolylbenzoxabismole (**1**) followed by self-condensation of hydroxybismuthine (**3**) gave the corresponding dibismuth oxide **2**, which was found by X-ray crystallographic analysis to exhibit a dimeric form with a novel ladder type by both inter- and intramolecular Bi−O interactions.*

Organobismuth compounds have attracted interest because of the Lewis acidity and the nontoxicity of the bismuth atom.[1] Trivalent organobismuth compounds with electronegative substituents, such as halogen and oxygen atoms, are well-known to behave as good Lewis acids and to form tetracoordinate structures easily by the coordination of Lewis bases.[1,2] The intermolecular interactions involving bismuth play an important role in the construction of supramolecular compounds, e.g., zigzag chain[3] and two-dimensional layer structures[4] with bismuth−halogen contacts as well as polymeric chains[5] and fused rings[6,7] with bismuth−oxygen interactions. The intramolecular version of the Bi−O interaction also serves to form Bi-containing small-ring structures, as shown in the cases of organobismuth compounds bearing carboxyl,[8] 2-methoxyphenyl,[9] or 2-(methoxymethyl)phenyl groups.[10] Although the molecular construction that takes advantage of the combination of multiple inter- and intramolecular Bi−O interactions is expected to provide unique ring systems such as poly-fused rings, poly-spiro rings, and their combinations, few examples of organobismuth compounds containing both interactions have been reported.[6] We report here the synthesis and structure of a dibismuth oxide with a novel ladder framework comprised of three 1,3,2,4-dioxadibismetane rings by taking advantage of both inter- and intramolecular Bi−O interactions.

The benzoxabismole $R_fBi(C_6H_4\text{-}4\text{-}CH_3)$ ($R_f = -C_6H_3\text{-}5\text{-}C(CH_3)_3\text{-}2\text{-}C(CF_3)_2O-$) (**1**), bearing the Martin ligand,[11] was prepared by a procedure similar to that used in the synthesis of the previously reported benzoxabismole.[12] The dibismuth oxide $(R_fBi)_2O$ (**2**) was obtained from **1** on standing in $CDCl_3-D_2O$ or $C_6D_6-D_2O$ at room temperature for 10 days in an NMR tube (Scheme 1) (see below). Treatment of benzoxabismole **1** with 1 M hydrochloric acid in $CHCl_3$ at room temperature for 8 h also gave **2** quantitatively.[13]

X-ray crystallographic analysis of **2**, obtained by recrystallization from hexane, showed a dimeric structure consisting two independent molecules of **2** (Figure 1).[14] The intermolecular distances Bi(2)−O(4) and Bi(3)−O(3) are 2.266(7) and 2.263(7) Å, respectively, which are notably shorter than the sum of the van der Waals

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(13) A $CHCl_3$ solution (8 mL) of 6-*tert*-butylbenzoxabismole (**1**; 95 mg, 0.16 mmol) was treated with 1 M aqueous HCl (2 mL) at room temperature under argon and stirred for 8 h. The reaction solution was extracted with $CHCl_3$ (10 mL × 3), washed with $Na_2CO_3(aq)$ (10 mL), and brine (10 mL), dried with $MgSO_4$, and evaporated in vacuo to give **2** as colorless solids (80 mg, 0.039 mmol, 98%). **2**: colorless crystals (from hexane); mp 320−325 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 0.95 (s, 9H, *t*-Bu), 1.36 (s, 9H, *t*-Bu), 7.33 (dd, $J = 8.5$, 2.0 Hz, 1H), 7.65 (dd, $J = 8.5$, 2.0 Hz, 1H), 7.95 (d, $J = 2.0$ Hz, 1H), 8.09 (d, $J = 8.5$ Hz, 1H), 8.14 (br d, $J = 8.5$ Hz, 1H), 9.19 (d, $J = 2.0$ Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 30.85 (s), 31.04 (s), 34.97 (s), 35.55 (s), 89.81 (sept, $J = 29$ Hz), 96.20 (sept, $J = 30$ Hz), 124.6 (q, $J = 288$ Hz), 124.7 (q, $J = 288$ Hz), 125.8 (s), 126.7 (s), 127.4 (q, $J = 289$ Hz), 127.8 (q, $J = 289$ Hz), 130.5 (s), 131.1 (s), 133.0 (s), 135.4 (s), 143.2 (s), 147.0 (s), 155.2 (s), 156.4 (s), 217.0 (s), 220.3 (s); ^{19}F NMR (254 MHz, $CDCl_3$) δ −77.7 (br d, $J = 7.2$ Hz, 3F), −77.4 (q, $J = 8.4$ Hz, 3F), −74.5 (br d, $J = 7.2$ Hz, 3F), −71.4 (q, $J = 8.4$ Hz, 3F); FAB-MS *m/z* 2005 (M × 2 − *t*-Bu), 1537, 1255, 1031 (M + H), 1015 ($M - CH_3$), 961 ($M - CF_3$), 732, 659, 507, 209 (Bi). Anal. Calcd for $C_{26}H_{24}Bi_2F_{12}O_3$: C, 30.31; H, 2.35. Found: C, 30.11; H, 2.53.

(14) Crystal data for dimer of **2**: $C_{52}H_{48}Bi_4F_{24}O_6$, fw = 2060.83, monoclinic, space group $C2/c$, $a = 26.7910(7)$ Å, $b = 19.4570(4)$ Å, $c = 23.8010(6)$ Å, $V = 12219.9(5)$ Å^3, $Z = 8$, $D_c = 2.240$ g cm^{-3}. The final cycle of full-matrix least-squares refinement was based on 3830 observed reflections ($I > 3.00\sigma(I)$) and 312 variable parameters and converged at R (R_w) = 0.059 (0.106). All calculations were performed using CrystalStructure, version 1.00, of Rigaku Corp. and Molecular Structure Corp.

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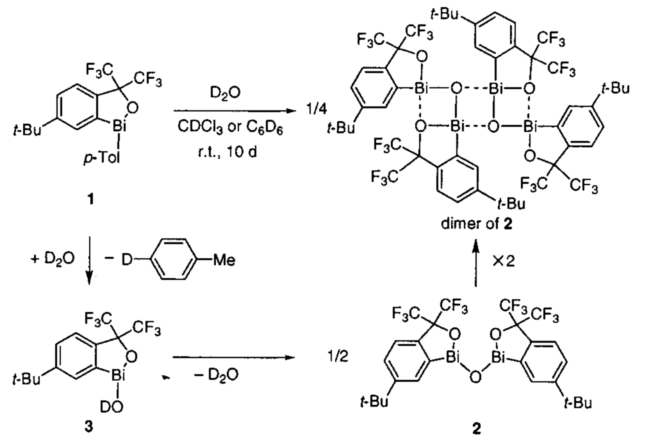
Scheme 1



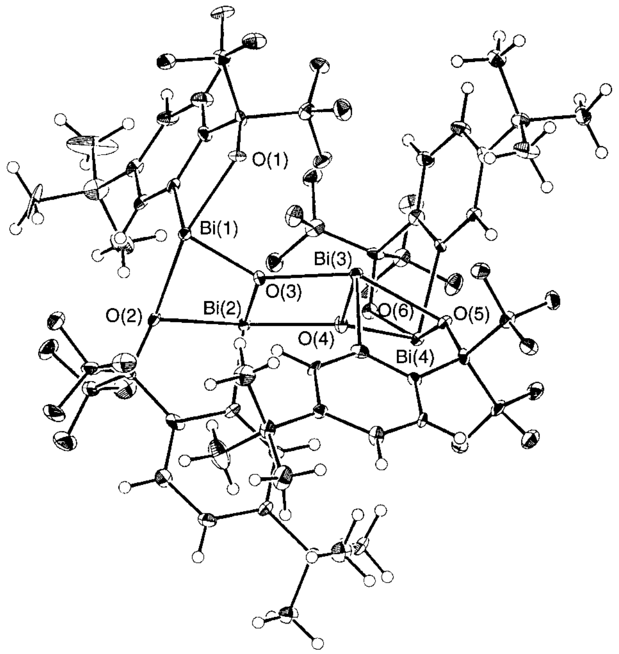


Figure 1. ORTEP drawing of **2** (30% probability). Selected bond lengths (Å), angles (deg), and torsion angles (deg): Bi(1)–O(1) = 2.183(7), Bi(1)–O(2) = 2.553(8), Bi(1)–O(3) = 2.096(7), Bi(2)–O(2) = 2.327(7), Bi(2)–O(3) = 2.176(8), Bi(2)–O(4) = 2.266(7), Bi(3)–O(3) = 2.263(7), Bi(3)–O(4) = 2.170(7), Bi(3)–O(5) = 2.362(7), Bi(4)–O(4) = 2.113(7), Bi(4)–O(5) = 2.546(8), Bi(4)–O(6) = 2.201(7), O(1)–Bi(1)–O(2) = 149.4(3), O(2)–Bi(2)–O(4) = 141.3(3), O(3)–Bi(3)–O(5) = 142.0(3), O(5)–Bi(4)–O(6) = 149.7(4), Bi(1)–O(2)–Bi(2)–O(3) = 20.4(7), Bi(2)–O(3)–Bi(3)–O(4) =3.2(0), Bi(3)–O(4)–Bi(4)–O(5) = 20.3(6).

radii (3.67 Å) and close to the sum of the covalent bond radii of these atoms (2.13 Å).[15] Such structural features apparently indicate the formation of a 1,3,2,4-dioxadibismetane ring,[16] i.e., a Bi(3)–O(3)–Bi(2)–O(4) ring. In each independent molecule of **2**, one oxygen atom of the Martin ligand coordinates to the bismuth atom intramolecularly to form Bi(1)–O(2) and Bi(4)–O(5) bonds, respectively. The corresponding bond lengths (2.553(8) and 2.546(8) Å, respectively) are somewhat longer than the intermolecular distances noted above but much shorter than the sum of their van der Waals radii, indicating strong Bi–O intramolecular coordination. This is the first example of such intramolecular coordination of the oxygen atom of the Martin ligand. These intramolecular Bi–O interactions also construct two 1,3,2,4-dioxadibismetane rings on both sides of the above-mentioned four-membered ring, eventually providing a ladder type framework which is composed of three 1,3,2,4-dioxadibismetane rings with *four rungs*, i.e., the Bi(1)–O(2), Bi(2)–O(3), Bi(3)–O(4), and Bi(4)–O(5) bonds, respectively. Taking into consideration the benzoxabismole units that stick to the outer dioxadibismetane rings, a dimer of **2** forms a unique multifused ring system comprised of three dioxadibismetane rings fused by two benzoxabismole rings. The central four-membered ring, Bi(2)–O(3)–Bi(3)–O(4), is almost planar, judging from the torsion angle of Bi(2)–O(3)–Bi(3)–O(4) (3.2(0)°) and the sum of the interior angles (359.8°), whereas both outer four-membered rings are slightly folded, as indicated by the torsion angles of Bi(1)–O(2)–Bi(2)–O(3) and Bi(3)–O(4)–Bi(4)–O(5) (20.4(7) and 20.3(6)°, respectively) and the sum of the interior angles (350.5 and 350.5°, respectively). The fused-ring system showed an anti-type twisted structure in the ladder framework: Bi(1) and O(5) atoms are located at 0.338 and 0.487 Å above and below the least-squares plane of the central dioxadibismetane ring, respectively. Each bismuth atom exhibits a distorted pseudo trigonal bipyramidal geometry with two oxygen atoms at apical positions and with a carbon atom, an oxygen atom, and a lone pair at the equatorial positions, respectively. The bond angles between each apical bond (141.3(3)–149.7(3)°) deviate from linearity to a remarkable extent. Such a deviation of apical bond angles often is observed in hypervalent compounds bearing the Martin ligand and a four-membered ring.[17] The deviation of the O(3)–Bi(3)–O(5) apical bond angle causes the O(5) atom to be located below the plane of the central dioxadibismetane ring. Oxygen O(2) at the symmetrical position with regard to the O(5) atom is located on a nearly similar plane of the central ring, while the Bi(1) atom is located above the plane, because of the steric congestion between two Martin ligands. The twisted structure of the fused-ring system is most likely explained by these structural deviations.

The molecular weight of **2** obtained by vapor pressure osmometry was 2.1 × 10^3, indicating that **2** exists as a dimer also in $CHCl_3$ solution. The ^1H and ^{19}F NMR spectra of **2**[13] in $CDCl_3$ at room temperature showed two sets (δ_H 0.95 and 1.36) of signals for both *tert*-butyl groups and four sets (δ_F −77.7, −77.4, −74.6, and −71.4) of quartets for the trifluoromethyl groups, respectively, also suggesting a dimeric structure similar to that in the crystal structure. Interestingly, two signals of the ortho proton of the aromatic ring of the Martin ligand in ^1H NMR spectra were observed at 8.14 and 9.19 ppm, which is a typical feature of a trigonal bipyramidal (TBP) or a pseudo-TBP structure of a compound bearing the Martin ligand.[18] In the ^{13}C NMR spectrum of **2** at

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room temperature, two peaks for the two different carbon atoms adjacent to the bismuth atoms were observed at much lower field, 216.9 and 220.3 ppm, respectively, compared to that of **1** (190.2 ppm). These downfield shifts are also characteristics for the carbons adjacent to a hypervalent central atom.[17−19] VT-^{1}H and ^{19}F NMR spectra in $C_2D_2Cl_4$ solutions showed no apparent change at 140 °C, indicating that these inter- and intramolecular Bi−O interactions are strong enough to be kept under the current conditions. In the FAB-MS spectrum, a fragment ion peak was observed at *m*/*z* 2005 [M × 2 − *t*-Bu] as well as *m*/*z* 1031 [M + H]. This result suggests that **2** exists as a dimeric structure even in the gas phase. Thus, **2** makes a good contrast with $[\{Bi[OCH(CF_3)_2]_3(thf)\}_2]$ existing as an equilibrium mixture between a monomer and a dimer at room temperature.[20]

The GC-MS and ^{1}H NMR spectra of the reaction mixture showed the molecular ion peak and signals due to 4-deuteriotoluene, respectively. Monitoring of the reaction solution by ^{1}H and ^{19}F NMR spectra did not show any peak other than those of **1**, **2**, and toluene. These results as well as the observed acceleration of the reaction by addition of HCl suggest that **2** should be formed by electrophilic aromatic substitution of **1** after coordination of water to the Lewis acidic bismuth atom and successive fast self-condensation of the resulting hydroxybismuthine **3**.[12]

We have shown the synthesis and structure of a novel organobismuth compound with a ladder-type structure consisting of both inter- and intramolecular Bi−O interactions, that is, a unique fused-ring system, in the crystalline and solution states. These results indicate that designs using a combination of both interactions are expected to achieve the construction of the novel molecular framework. Further work is in progress to construct supramolecular compounds by taking advantage of both inter- and intramolecular Bi−O interactions.

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Supporting Information Available: Text giving the experimental procedures for the preparation and spectral data of **1** and tables giving crystal data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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