Oxidation of Me_3Bi with Formation of the Inorganic Polymer $[Me_2BiOMe]_\infty$

Hans Joachim Breunig, Enno Lork,
and Mihai-Gabriel Nema

Institut für Anorganische und Physikalische Chemie,
Fachbereich 2 der Universität Bremen,
Postfach 330 440, 28334 Bremen, Germany

Reprint requests to Prof. Dr. H. J. Breunig.
Fax: 0049-421-218-4042. E-mail: hbreunig@uni-bremen.de

Z. Naturforsch. **2009**, *64b*, 1213 – 1214;
received August 5, 2009

Single crystals of $[Me_2BiOMe]_\infty$ (**1**) formed in the reaction of Me_3Bi with oxygen in benzene have been analysed by X-ray crystallography (orthorhombic, *Pnma*, $Z = 4$, $a = 8.254(2)$, $b = 9.9020(10)$, $c = 7.0430(10)$ Å, $T = 173(2)$ K).

Key words: Bismuth, Alkoxides, X-Ray Crystallography

Introduction

The chemistry of diorganylbismuth alkoxides has received little attention despite their potential as precursors for important bismuth oxide-based materials [1 – 3]. Et_2BiOEt was proposed as an intermediate in the oxidation of Et_3Bi and was prepared independently by the reaction of Et_2BiBr with NaOEt [4]. The first compounds of the type R_2BiOR with known crystal structures are the aryl derivatives $[Et_2BiOR]_\infty$ (R = C_6F_5, Ph) formed by reactions of Et_3Bi with the phenols ROH. In the crystalline state they exist as helical chains in which bridging phenoxides join Et_2Bi groups [5]. We report here on the formation and crystal structure of the dialkylbismuth alkoxide $[Me_2BiOMe]_\infty$ (**1**) by reaction of Me_3Bi with oxygen. Little is known of this type of reactions in organo bismuth chemistry, but related reactions of oxygen with alkyl derivatives of zinc, aluminium or other metals leading to metal alkoxides, alkylperoxides, or carboxylates have been studied frequently [6 – 8].

Results and Discussion

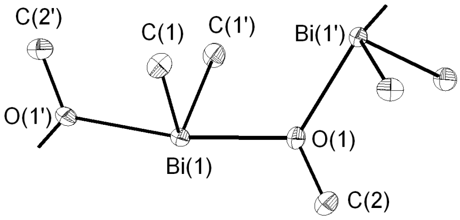

Fig. 1. Displacement ellipsoid representation (50 %) of a fragment of the $[Me_2BiOMe]_\infty$ chain (**1**) showing the environment of bismuth and oxygen. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Bi(1)–C(1) 2.243(6), Bi(1)–C(1′) 2.243(6), Bi(1)–O(1) 2.359(6), Bi(1)–O(1′) 2.344(6), O(1)–C(2) 1.390(10); C(1)–Bi(1)–C(1′) 96.3(4), C(1)–Bi(1)–O(1′) 87.50(19), C(1′)–Bi(1)–O(1′) 87.50(19), C(1)–Bi(1)–O(1) 86.04(19), C(1′)–Bi(1)–O(1) 86.04(19), O(1′)–Bi(1)–O(1) 170.30(13), Bi(1)–O(1)–C(2) 115.5(6), Bi(1)–O(1′)–C(2′) 121.2(6), Bi(1′)–O(1)–Bi(1) 123.4(3).

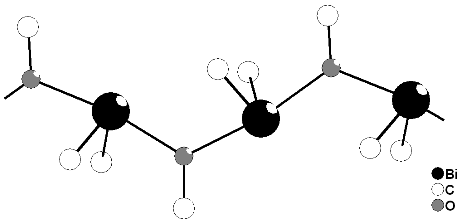

Fig. 2. View of a section of the polymeric chain of **1**.

Slow admission of air to a solution of Me_3Bi in C_6D_6 in an NMR tube for 12 h at r. t. gives colourless crystals of $[Me_2BiOMe]_\infty$ (**1**). **1** is an air-sensitive solid almost insoluble in organic solvents. The solubility in benzene is not sufficient for the observation of NMR spectra. Also the volatility of **1** is very low. Mass spectra do not show signals of the monomeric unit of **1**. Instead signals of the decomposition product Me_3Bi are observed. The structure of **1** was determined by single crystal X-ray diffractometry. Sections of the polymeric chain are depicted in Figs. 1 and 2.

The coordination geometry at the bismuth atom corresponds to a seesaw structure (*i. e.* a trigonal bipyramid with a vacant equatorial site) in which the bridging methoxide ligands occupy the axial positions. The two methyl groups are situated in the equatorial plane. The Bi atom is hypervalent and can be described as a 10-Bi-4 system in the N–Bi–L designation (N = number of valence electrons at bismuth, L = number of ligands). The Bi–O bond lengths in **1** (2.359(6), 2.344(6) Å) are shorter than in $Et_2BiOC_6F_5$ (2.4105(7) Å) and $Et_2BiOC_6H_5$ (2.382(7) Å). All these bond lengths are larger than the sum of the covalent radii of Bi and O (Σr_{cov} Bi–O 2.18 Å) thus reflecting the hypervalent nature of these bismuth oxygen polymers. The O–Bi–O (170.30(13)°) and Bi–O–Bi (123.4(3)°) angles in **1** are smaller than the corresponding values of $Et_2BiOC_6F_5$ (O–Bi–O 179.54(4), Bi–O–Bi 113.57(3)°), or $Et_2BiOC_6H_5$ (O–Bi–O 179.0(3), Bi–O–Bi 115.4(5)°). The C–Bi–C angles in the structure of **1** (96.3(4)°) are wider than in $Et_2BiOC_6F_5$ (80(2)°) and $Et_2BiOC_6H_5$ (81.2(9)°). In contrast to the helical arrangements of $[Et_2BiOR]_\infty$ (R = C_6F_5, Ph) the structure of **1** corresponds to a zig-zag chain system with alternating bismuth and oxygen atoms lying in the same plane [Bi(1′)–O(1)–Bi(1)–O(1′) 0°]. A closely related structure is that of the polymeric azide $[Me_2BiN_3]_\infty$ [9].

Experimental Section

Synthesis of $[Me_2BiOMe]_\infty$ (1)

Slow admission of air to a solution of 0.25 g (0.4 mmol) Me_3Bi [10] in C_6D_6 in an NMR tube for 12 h at r. t. gave (0.11 g, 45 %) colourless crystals of $[Me_2BiOMe]_\infty$ (**1**). M. p. 188 – 190 °C. – IR (Nujol): ν = 1154, 1032, 971, 890, 722, 605, 559, 496, 467 cm^{-1}. – MS (EI 70 eV): *m/z* (%) = 254 (60) $[Me_3Bi]^+$, 239 (100) $[Me_2Bi]^+$, 224 (60), 209 (70) $[Bi]^+$.

X-Ray structure determination

A suitable single crystal of **1** mounted on a glass fibre using KelF oil was investigated under a cold nitrogen stream on a Siemens P4 diffractometer. Crystal data: C_3H_9BiO, Mr = 270.08, crystal size 0.9 × 0.1 × 0.1 mm^3, orthorhombic, *Pnma*, $Z = 4$, $a = 8.254(2)$, $b = 9.902(1)$, $c = 7.043(1)$ Å, $V = 575.63(17)$ Å^3, $D_{calcd} = 3.116$ g cm^{-3}, $\mu(MoK_\alpha) = 30.478$ cm^{-1}, $T = 173(2)$ K. Data collection and refinement: graphite monochromator, MoK_α radiation, $\lambda = 0.71073$ Å, $F(000) = 472$ e, 1747 measured reflections, 697 independent reflections ($R_{int} = 0.0348$), 657 reflections with $I \geq 2\,\sigma(I)$, *hkl* range −1/+10, ±12, −1/+9, $\theta_{max} = 27.50°$, empirical (DIFABS) absorption correction [11]. The structure was solved using Direct Methods and refined using full-matrix least-squares methods on F^2. The hydrogen atoms were included in riding positions with isotropic thermal parameters set at 1.2 times those of the carbon atoms to which they are directly attached. Final R values for $I \geq 2\,\sigma(I)$: $R(F) = 0.0248$, $wR(F^2) = 0.0604$; all data: $R(F) = 0.0270$, $wR(F^2) = 0.0613$, Goof$(F^2) = 1.062$, residual electron densities: 1.31 and −2.10 e Å^{-3}. All calculations were carried out using the SHELX package [12].

CCDC 740846 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

We thank the Deutsche Forschungsgemeinschaft for financial support.

---

[1] H. Suzuki, Y. Matano, *Organobismuth Chemistry*, Elsevier, Amsterdam, **2001**.

[2] M. Mehring, *Coord. Chem. Rev.* **2007**, *251*, 974 – 1006.

[3] C. Silvestru, H. J. Breunig, H. Althaus, *Chem. Rev.* **1999**, *99*, 3277 – 3327.

[4] G. Calingaert, H. Soroos, V. Hnizda, *J. Am. Chem. Soc.* **1942**, *64*, 392 – 397.

[5] K. H. Whitmire, J. C. Hutchison, A. L. McKnight, C. M. Jones, *J. Chem. Soc., Chem. Commun.* **1992**, 1021 – 1022.

[6] J. Lewinski, W. Shiwinski, M. Dranka, I. Justyniak, J. Lipkowski, *Angew. Chem.* **2006**, *118*, 4944 – 4947; *Angew. Chem. Int. Ed.* **2006**, *45*, 4826 – 4829.

[7] S. Jana, R. J. F. Berger, R. Fröhlich, T. Pape, N. W. Mitzel, *Inorg. Chem.* **2007**, *46*, 4293 – 4297.

[8] J. Lewinski, M. Koscielski, K. Suwala, I. Justyniak, *Angew. Chem.* **2009**, *121*, 7151 – 7154; *Angew. Chem. Int. Ed.* **2009**, *48*, 7017 – 7020.

[9] J. Müller, U. Müller, A. Loss, J. Lorberth, H. Donath, W. Massa, *Z. Naturforsch.* **1985**, *40b*, 1320 – 1326.

[10] O. Scherer, P. Hornig, M. Schmidt, *J. Organomet. Chem.* **1966**, *6*, 259 – 264.

[11] N. Walker, D. Stuart, *Acta Cryst.* **1983**, *A39*, 158 – 166.

[12] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112 – 122.

Druck: AZ Druck und Datentechnik GmbH, Kempten