Oxidation of Me₃Bi with Formation of the Inorganic Polymer [Me₂BiOMe]ₙ

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Single crystals of [Me₂BiOMe]ₙ (1) formed in the reaction of Me₃Bi 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]. Et₂BiOEt was proposed as an intermediate in the oxidation of Et₃Bi and was prepared independently by the reaction of Et₂BiBr with NaOEt [4]. The first compounds of the type R₂BiOR with known crystal structures are the aryl derivatives [Et₂BiOR]ₙ (R = C₆F₅, Ph) formed by reactions of Et₃Bi with the phenols ROH. In the crystalline state they exist as helical chains in which bridging phenoxides join Et₂Bi groups [5]. We report here on the formation and crystal structure of the dialkylbismuth alkoxide [Me₂BiOMe]ₙ (1) by reaction of Me₃Bi 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, alkyloxides, or carboxylates have been studied frequently [6 – 8].

Results and Discussion

Slow admission of air to a solution of Me₃Bi in C₆D₆ in an NMR tube for 12 h at r. t. gives colourless crystals of [Me₂BiOMe]ₙ (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 Me₃Bi are observed. The structure of 1 was determined by single crystal X-ray diffractionometry. 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 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 Et₂BiOC₆F₅ (2.4105(7) Å) and Et₂BiOC₆H₅ (2.382(7) Å). All these bond lengths are larger than the sum of the covalent radii of Bi and O (Σr⁺ 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 Et₂BiOC₆F₅ (O–Bi–O 179.54(4), Bi–O–Bi 113.57(3)°), or Et₂BiOC₆H₅ (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 Et₂BiOC₆F₅ (80(2)°) and Et₂BiOC₆H₅ (81.2(9)°). In contrast to the helical arrangements of [Et₂BiOR]∞ (R = C₆F₅, 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 [Me₂BiN₃]∞ [9].

Experimental Section

Synthesis of [Me₂BiOMe]∞ (1)

Slow admission of air to a solution of 0.25 g (0.4 mmol) Me₂Bi [10] in C₄H₄ in an NMR tube for 12 h at r.t. gave (0.11 g, 45 %) colourless crystals of [Me₂BiOMe]∞ (1). M.p. 188 – 190 °C. – IR (Nujol): 2923, 2855, 1433, 1387, 1350, 1293, 1079, 722, 605, 559, 496, 467 cm⁻¹. – MS (EI 70 eV): m/z (%) = 254 (60) [Me₂Bi]⁺, 239 (100) [Me₂Bi]⁺, 224 (60), 209 (70) [Bi]⁺.

X-Ray structure determination

A suitable single crystal of 1 mounted on a glass fibre using KClO₄ was investigated under a cold nitrogen stream on a Siemens P4 diffractometer. Crystal data: C₃H₉BiO, Mr = 270.08, crystal size 0.9 × 0.1 × 0.1 mm³, orthorhombic, Pnma, Z = 4, a = 8.254(2), b = 9.902(1), c = 7.043(1) Å, V = 575.63(17) Å³, Dcalc = 3.116 g cm⁻³, μ(MoKα) = 30.478 cm⁻¹, T = 173(2) K. Data collection and refinement: graphite monochromator, MoKα radiation, λ = 0.71073 Å, F(000) = 472 e, 1747 measured reflections, 697 independent reflections (Rint = 0.0348); 657 reflections with I ≥ 2 σ(I); hkl range −1/+10, ±12, −1/+9, θmax = 27.50°. Empirical (DIFABS) absorption correction [11]. The structure was solved using Direct Methods and refined using full-matrix least-squares methods on F². 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 ≥ 2 σ(I): R(F) = 0.0248, wR(F²) = 0.0604; all data: R(F) = 0.0270, wR(F²) = 0.0613. Goof(F²) = 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.

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