

Synthesis and Structure of $[\text{Et}_2\text{Bi}(\text{OAr})]_\infty$ (Ar = C_6F_5 , Ph): a New Inorganic Chain Polymer

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Triethylbismuth reacts slowly with HOAr (Ar = C_6F_5 , Ph) in refluxing toluene to yield the compounds $[\text{BiEt}_2\text{OAr}]_\infty$ which are shown by single crystal X-ray diffraction to exist as chiral chain polymers in which bridging alkoxides join Et_2Bi groups containing a stereoactive lone pair of electrons.

Main group alkoxides and alkyl complexes are receiving considerable attention due to their potential application as precursors to a variety of important electronic materials. For chemical vapour deposition and sol-gel methodologies volatile and/or soluble species are desirable. Bismuth in particular is of interest as a component to several superconducting phases. It was not until very recently that the first bismuth tris-alkoxides were structurally characterized¹ even though they had been first reported in the 1960s.² $\text{Et}_2\text{Bi}(\text{OEt})$ was proposed as an intermediate in the oxidation of Et_3Bi and was prepared independently by the reaction of Et_2BiBr with NaOEt .³ No structural data, however, is available for this compound.

In order to expand the scope of the synthetic strategies for bismuth alkoxides, we have been examining the reactions of alkyl and aryl bismuth complexes with various alcohols and wish to report the synthesis and structures of $[\text{Et}_2\text{Bi}(\text{OAr})]_\infty$ (**1**, Ar = C_6F_5 ; **2** Ar = Ph), the first mixed R-OR bismuth compounds to be structurally characterized.

Gilman and Nelson⁴ reported that HOAr and Et_3Bi did not react at 100 °C after 30 min of reaction time, but refluxing Et_3Bi with excess HOAr for 40 h in toluene, followed by removing the solvent under vacuum, afforded well-formed crystals or powders of **1** or **2**.[‡] In spite of the excess HOAr, only one Et group on the bismuth was replaced. The mass spectra of **1** and **2** show parent ions corresponding to the monomeric $\text{Et}_2\text{Bi}(\text{OAr})$. In both cases fragments corresponding to BiEt_2 , BiEt and Bi were also observed. The compounds were subjected to single crystal X-ray analyses.[§] **1** and **2** are isomorphous, being composed of chiral helical chains (Fig. 1) of alternating Bi and O atoms which lie about the crystallographic three-fold screw axes with the BiEt_2 and OAr groups situated on crystallographic two-fold axes. The unique Bi-O distances are 2.4105(7) for **1** and 2.382(7) Å for **2**. The Et groups and Ar functions point away from the centroid of the spiral so that the Ar functions are situated almost parallel to the C faces of the crystal lattice (Fig. 2). As a result the crystal lattices of **1** and **2** have nearly identical *c* spacings while the *a*

distance in **1** is ca. 0.6 Å longer in order to accommodate the fluorine atoms. The solubilities of **1** and **2** in organic solvents and the NMR data for **1** indicate that these complexes are monomeric or rapidly exchanging oligomers in solution.

The coordination geometry at the bismuth atom is best described as a see-saw structure (*i.e.* trigonal bipyramid with an equatorial site occupied by a lone pair of electrons) in which the bridging phenoxide ligands occupy the axial positions. Thus, the Bi atom is a 'hypervalent' ten-electron centre. The O-Bi-O angles are: **1**, 179.54(4); **2**, 179.0(3)°, while the Bi-O-Bi angles are: **1**, 113.57(3); **2**, 115.4(5)°. The two Et groups and the stereochemically active lone pair of electrons are situated in the equatorial plane with $\angle\text{C-Bi-C}$ angles of 80(2)° for **1** and 81.2(9)° for **2**. This angle is particularly acute compared with the value of slightly less than 120° expected for this geometry by valence shell electron pair repulsion theory. A strikingly similar coordination geometry has been observed for $\beta\text{-Bi}_2\text{O}_3$ where the comparable equatorial-equatorial and axial-axial angles are 82.4 and 172.1°, respectively.⁵ The coordination complex $\text{Rb}[\text{Bi}(\text{SCN})_4]$ ⁶ has a similar arrangement of ligands but there the corresponding angles are 92.6 and 158.2°. It should be noted that the Et groups exhibit a common form of disorder at the β -carbons in both cases as indicated by a slightly larger thermal parameter, and the bond metrics involving these atoms are consequently not very accurate.

The reaction of BiPh_3 with HOC_5F_5 proceeds in refluxing toluene with removal of the phenyl rings giving dimeric

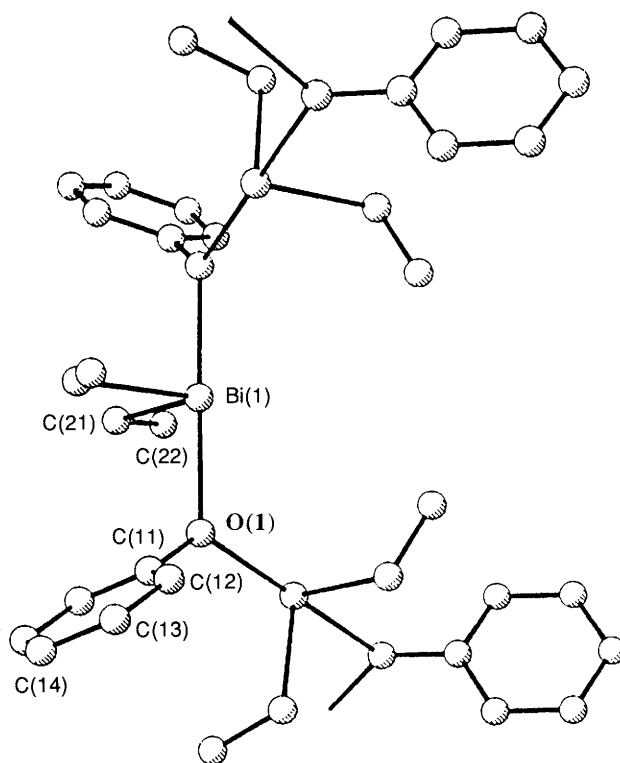


Fig. 1 PLUTO diagram of a segment of the chain polymer $[\text{Et}_2\text{Bi}(\text{OC}_6\text{F}_5)]_\infty$. The fluorine atoms have been omitted for clarity.

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‡ Analytical data for **1**: m.p. 166–168 °C; ¹⁹F NMR (C_6D_6 , ref. $\text{CF}_3\text{CO}_2\text{H}$), δ –98.95 (br), –91.22 (t) and –87.12 (dd) (1:2:2); ¹H NMR δ 2.55 (t) and 1.60 (br unresolved multiplet) (3:2); ¹³C NMR (C_6D_6 , 25 °C) δ 57.64 and 8.99 (Et), the ¹³C signals for the C_6F_5 group were not observed. Satisfactory elemental analyses have not yet been obtained due to the air and moisture sensitivity of the compound. For **2**: m.p. 174 °C. Satisfactory elemental analyses and clean spectral data have not yet been obtained due to the extreme air and moisture sensitivity of the compounds.

§ Crystal data for **1**: acentric trigonal space group $P3_221$ (No. 154), $T = -50$ °C, $a = 9.898(2)$, $c = 11.175(5)$ Å, $V = 948.2(6)$ Å³, $R = 0.0479$, $R_w = 0.0497$, $S = 1.660$, no. variables = 37, no. reflections observed [$I \geq 3\sigma(I)$] = 887. For **2**: acentric trigonal space group $P3_121$ (No. 152), $T = -50$ °C, $a = 9.326(3)$, $c = 11.160(6)$ Å, $V = 840.6(7)$ Å³, $R = 0.0359$, $R_w = 0.0385$, $S = 1.275$, no. variables = 40, no. reflections observed [$I \geq 3\sigma(I)$] = 924. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

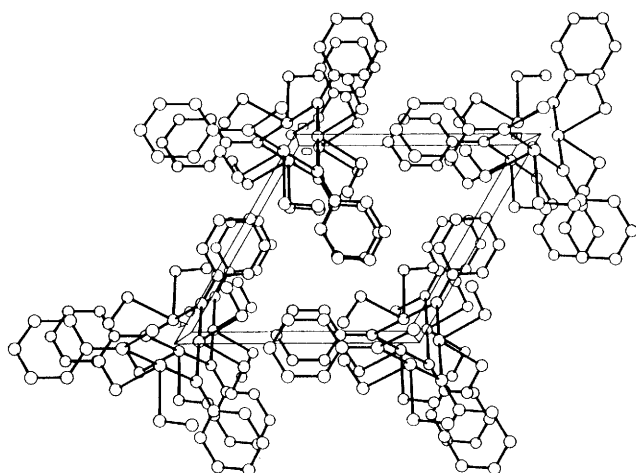


Fig. 2 Packing diagram showing the arrangement of the helical chains in the $[\text{Et}_2\text{Bi}(\text{OC}_6\text{F}_5)]_\infty$ structures. The fluorine atoms have been omitted for clarity.

$[\text{Bi}(\text{OC}_6\text{F}_5)_2(\mu\text{-OC}_6\text{F}_5)(\text{toluene})]_2$.⁷ It is curious that all three of the organic functions in BiPh_3 are replaced while only one in BiEt_3 is since the Bi-C(aryl) bond strength appears to be greater than that of Bi-C(alkyl).⁸ Work is in progress to

determine the generality of the reactivity and structural patterns observed here.

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