Molecular Precursors of Bismuth Oxide. Synthesis and Structure of $[Bi_2(\mu_2\text{-}OC_2H_4OMe)_4(OC_2H_4OMe)_2]_\infty$, a One-dimensional Ribbon-like Chain

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Compounds $[Bi(OBu^t)_3]_\infty$ and $[Bi_2(\mu_2\text{-}OC_2H_4OMe)_4(OC_2H_4OMe)_2]_\infty$ have been obtained by metathesis reactions between bismuth halides and the appropriate alkali alkoxides; *X*-ray structure analysis shows a one-dimensional extended 'skew' chain structure based on dimeric asymmetric $Bi_2(OC_2H_4OMe)_6$ units in which the metal displays a pyramidal tetragonal surrounding, with a small number of additional neighbours.

Bismuth(III) oxides are involved in various advanced materials such as superconductors[1] or photorefractive systems.[2] These materials have generally been obtained by traditional high-temperature solid-state reactions. Molecular precursors of Bi^{III} oxides remain rather limited, although they are of value for coatings, through either sol-gel or MOCVD techniques. A commercially available alkoxide formulated as $Bi(OEt)_3$ has already been used for low-temperature routes to Bi–Sr–Ca–Cu–O materials.[3] However, alkoxides $Bi(OR)_3$ (R = Me, Et, Pr^i),[4] reported to form in high yield by metathesis reaction between the trichloride and alkali alkoxides, are poorly characterized.

We report the synthesis of $Bi(OBu^t)_3$ and of $Bi(OC_2H_4OMe)_3$ as well as complete structural characterization of the latter. This highly soluble compound appears to be a one-dimensional polymer based on dinuclear asymmetric $Bi_2(\mu_2\text{-}OC_2H_4OMe)_4(OC_2H_4OMe)_2$ units in the solid.

The Bi^{III} alkoxides were obtained in good yields (~50%) by reaction between $BiCl_3$ or $BiBr_3$ and sodium t-butoxide or sodium methoxyethanolate (ratio 1:3) in tetrahydrofuran (THF). The good volatility of $Bi(OBu^t)_3$ (**1**)† allows its isolation and purification by sublimation (80—100 °C, 10^{-2} mmHg), but although it is more soluble than the Bi^{III} alkoxides reported so far, its solubility is moderate, even in polar solvents. Functional alcohols are largely used as additives in the sol-gel process, as a means of maintaining a homogeneous medium.[5] Bismuth tris(methoxyethanoate), $Bi(OC_2H_4OMe)_3$ (**2**)†‡ is highly soluble (even in pentane) and is obtained by extraction of the crude reaction product by diethyl ether.

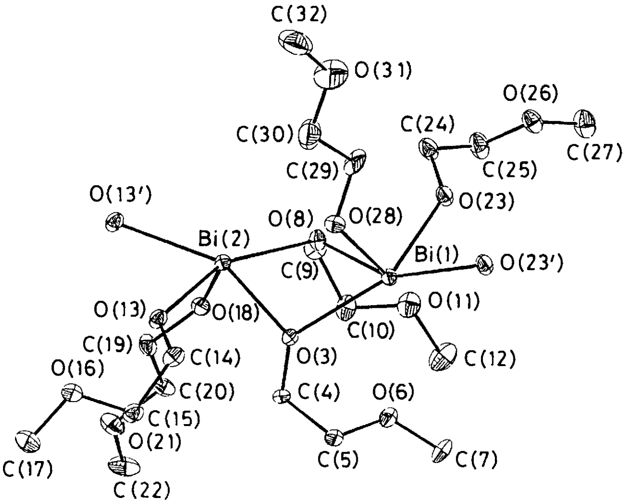

Figure 1. ORTEP view of the asymmetric $[Bi_2(OC_2H_4OMe)_6]$ subunit showing the atom numbering scheme. Important bond distances (Å) and angles (°): Bi(1)···Bi(2) 3.6426(4), Bi(1)···Bi(1') 3.9626(6), Bi(2)··· Bi(2') 3.9501(6), Bi(1)–O(8) 2.210(7), Bi(2)–O(8) 2.526(7), Bi(1)–O(3) 2.573(6), Bi(2)–O(3) 2.230(6), Bi(1)–O(23) 2.200(7), Bi(1)–O(23') 2.513(7), Bi(2)–O(13) 2.224(7), Bi(2)–O(23') 2.513(7), Bi(1)–O(28) 2.114(6), Bi(2)–O(18) 2.071(6), Bi(2)–O(3)–Bi(1) 98.4(2), Bi(2)–O(8)–Bi(1) 100.3(2), O(3)–Bi(1)–O(8) 72.5(2), O(3)–Bi(2)–O(8) 73.2(2), Bi–O–C (av.) 121.8. Atoms labelled ' are related by an inversion centre.

X-Ray diffraction studies were carried out on both compounds; however, although a linear arrangement of the metal atoms could be established for (**1**), its complete structural characterization could not be achieved. Compound (**2**) displays a chain structure as well. At first approximation all bismuth atoms are pentaco-ordinated (Figure 1), with bismuth alkoxo bond lengths ranging from 2.071(6) to 2.573(6) Å. The metals have a distorted tetragonal pyramidal surrounding; the lone pair is stereochemically active, and appears to be directed opposite to the apical alkoxo group. The overall structure can thus be viewed as a polymerisation of MX_3 units to a chain of MX_5 pyramids *trans* fused at a basal edge. The terminal alkoxo bonds are, as expected, the shortest ones. The metal atoms are connected by unsymmetrical alkoxo bridges of 2.226, 2.524 Å and 2.205, and 2.542 Å for Bi(1) and Bi(2) respectively. The

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† *Selected spectroscopic data* for (**1**), $[Bi(OC_4H_9)_3]_\infty$: IR (mineral oil) ν(Bi–OR) 572, 550, 459 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39; EI MS (*m/z*), M = $Bi(OBu^t)_3$, M–Me (24%), M–OBu^t (48%), $BiOH(OBu^t)$ (31%), BiC_4H_6 (49%), $BiOC_3H_2$ (4%), BiOMe (2%), BiOH (15%), Bi (37%), C_4H_9 (100%). For (**2**), $[Bi_2(OC_2H_4OMe)_6]_\infty$; IR (mineral oil) ν(Bi–O) 583, 524 cm^{-1}; ^1H NMR ($CDCl_3$, 10^{-3} M) δ 3.41, 3.39s, 3.37s (Me), 3.50—3.54m, 3.7—3.77m (CH_2); $^{13}C\{^1H\}$ NMR (C_6D_6, 0.15 M) δ 58.4, 58.6 (Me), 62.6, 63.1, 63.5, 71.7, 71.9, 77.7 (CH_2). Monocrystals were obtained by slow cooling of diethyl ether solutions. Both compounds gave satisfactory elemental analyses.

‡ *Crystal data* for (**2**): $C_{18}H_{42}O_{12}Bi_2$, M = 868; triclinic, space group $P\bar{1}$, a = 10.726(3), b = 14.425(3); c = 12.018(2) Å, α = 93.44(2), β = 113.66(2), γ = 119.56(2)°, U = 1401 Å^3, D_c = 2.06 g cm^{-3} for Z = 2, μ(Mo-K_α) = 125.7 cm^{-1}. 6415 Data were collected at low temperature (−160 °C) on an Enraf-Nonius CAD-4 diffractometer. Instrumental problems which occurred after collection of half of the data led to the collection of the remaining data on another crystal of approximately the same size. Bismuth atoms were found using SHELXS.[6] All remaining non-hydrogen atoms were located on successive difference electron density maps. The structure was refined by least-squares techniques with approximation (in three blocks) to the normal matrix using CRYSTALS.[7] 4070 Reflections with $I > 3\sigma(I)$ were used to solve and refine the structure: R = 0.0370, R_w = 0.0432, 299 variables. Of the two terminal alkoxo groups, one is disordered. This disorder affects the oxygen atom of the ether functionality which is statistically distributed on two sites separated by 0.8 Å. Anomalous dispersion terms were used. Empirical absorption correction using DIFABS[8] was applied. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

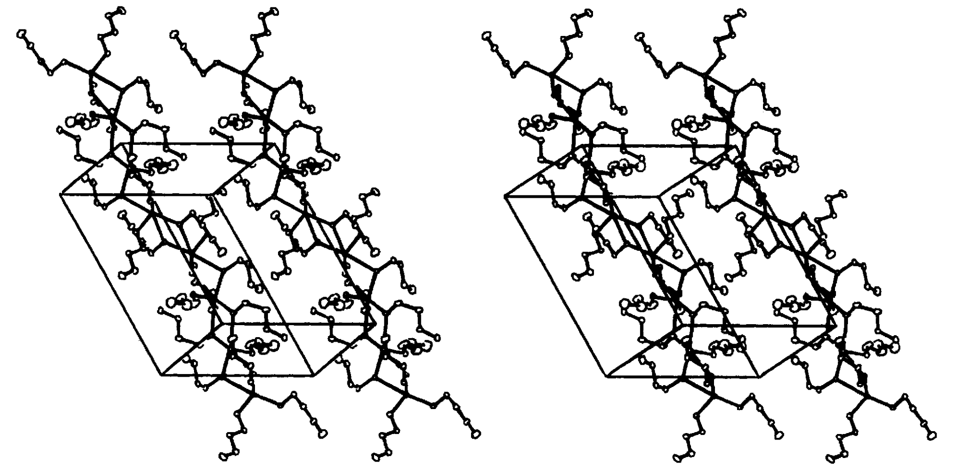

Figure. 2. Stereoview showing the extended chain structure along the *b* axis. For clarity, only two chains have been represented.

Bi–O–C angles range from 117.0(6) to 126.1(6)°; they are quite small and thus in agreement with the rather long Bi alkoxo bonds.

Additional neighbours, however, finally give a different surrounding for the two bismuth atoms: Bi(1) is pseudo-octaco-ordinated, while Bi(2) is only heptaco-ordinated. The 'apical' alkoxo moiety linked to Bi(1) interacts with Bi(2) in a semi-bridging manner [Bi–O 2.924(6) Å], while the ether functionality of the bridging alkoxo groups provides further rather close oxygen neighbours for the metals [short contacts between O(16′) and Bi(2), and between O(6), O(11), O(26′), and Bi(1)], directed toward the lone pair as well. The Bi–O(Me) distances, ranging from 2.90 to 3.10 Å, are longer than those observed previously, in this laboratory, for yttrium compounds[9] in which the 2-methoxyethoxo groups act as authentic η^2-bridging chelating ligands, but significantly shorter than the sum of the van der Waals radii (3.47 Å). Structural data on bismuth(III) molecular derivatives with oxygen ligands remain scarce,[10] but most mixed Bi^{III} oxides have five or six neighbours at distances ranging from 2.1 to 2.7 Å,[11] and a small number of additional neighbours.

The chains are thus built up from dimeric asymmetric $Bi_2(\mu_2\text{-}C_2H_4OMe)_4(OC_2H_4OMe)_2$ units (Figure 1) which are linked to each other through bridging alkoxo oxygen atoms O(13) and O(23), arranged around inversion centres 0,0,0 [Bi(1) ··· Bi(1′) and 0, 1/2, 0 [Bi(2) ··· Bi(2′)]. Figure 2 shows the packing with the 'zigzag' like chains extended along the *b* axis. Metal–metal distances between these dimers along the chains, Bi(1) ··· Bi(1′) 3.9626(6) and Bi(2) ··· Bi(2′) 3.9501(6) Å, are significantly longer than the Bi(1) ··· Bi(2) bond lengths of 3.6426(4) Å observed within the dimeric unit.

The geometry of the bridge within the dimeric unit is non-planar. The bridge is folded around the O(3) ··· O(8) edge with a dihedral angle of 142.5°. By contrast, the bridges which ensure the extended chain structure are planar. Strain in the bridge is evidenced by the reduction of the bridge angles at Bi from the ideal 90° (72.8° average within the dimeric unit and 67.5° along the infinite chain). While bridging alkoxo groups are fairly common, strongly disymmetric bridges have so far, to our knowledge, not been reported, even though the overall structure of the bismuth derivative is somewhat related to that of $[VO(OMe)_3]_\infty$.[12] Such infinite 'skew' chains, however, have been observed for bismuth halide derivatives such as $(BiX_4)_\infty{}^{n-}$ (X = Cl, Br),[13] although the environment of the metal is octahedral.

By contrast with other bismuth alkoxides, bismuth tris-(methoxyethanolate) appears to be highly soluble, NMR spectra were found to be a function of the dilution (range 10^{-1}—10^{-3} mol dm^{-3}), and thus account for the presence of different species in solution. Equilibrium between various oligomers and/or isomers involving η^1- and η^2-co-ordination modes of the functional alkoxo moiety, is the most plausible explanation. Molecular weight data measurements taken in concentrated benzene solutions (0.1 mol dm^{-3}) by the Signer method[14] favour the dimeric species ($M_{\text{expt.}}$ 810 ± 80; $M_{\text{calc.}}$ 434).

The large solubility of $[Bi_2(\mu_2\text{-}OC_2H_4OMe)_4(OC_2H_4OMe)_2]_\infty$ is attractive for its use in sol-gel or pyrosol processes of mixed oxides, and experiments along this line are in progress.

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