

**Novel Aryloxybismuthoxide Clusters: X-Ray Crystal Structures of  $\text{Bi}_6(\mu_3\text{-O})_7(\mu_3\text{-OC}_6\text{F}_5)\{\text{Bi}(\text{OC}_6\text{F}_5)_4\}_3(\text{thf})_2$  and  $\text{Bi}_6(\mu_3\text{-O})_7(\mu_3\text{-OC}_6\text{F}_5)\{\text{Bi}(\text{OC}_6\text{F}_5)_4\}_3\cdot 2\text{C}_7\text{H}_8$  (thf = tetrahydrofuran)**

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Two complex cluster compounds containing octahedral  $[\text{Bi}_6(\mu_3\text{-O})_7(\mu_3\text{-OC}_6\text{F}_5)]^{3+}$  cores have been structurally characterized.

Metal alkoxide compounds have been receiving renewed attention as precursors to high temperature superconductors *via* sol-gel or vapour-deposition processes. Bismuth is an important component in several high  $T_c$  superconductors such as  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8^{1a}$  as well as the non-copper containing  $\text{Ba}_{0.65}\text{K}_{0.35}\text{BiO}_3$ .<sup>1b</sup> Details of the conversions of bismuth alkoxide compounds into oxides are not yet known. We report here the structural characterization of two complex aryloxy-bismuthoxide cluster compounds arising from the degradation of bismuth pentafluorophenoxide complexes.

We have previously reported the refluxing triphenylbismuth and three equivalents of pentafluorophenol in toluene cleanly affords the trisubstituted dimer **1**,  $[\text{Bi}(\text{OC}_6\text{F}_5)_3(\text{tol})]_2\cdot 2\text{tol}$ , in high yield.<sup>2a</sup> Recrystallization of **1** from tetrahydrofuran (thf) produces  $[\text{Bi}(\text{OC}_6\text{F}_5)_3(\text{thf})_2]_2$ , **2**.<sup>2b</sup> However, refluxing triphenylbismuth and three equivalents of pentafluorophenol in thf produced a small crop of fragile colourless plates of  $\text{Bi}_6(\mu_3\text{-O})_7(\mu_3\text{-OC}_6\text{F}_5)\{\text{Bi}(\text{OC}_6\text{F}_5)_4\}_3(\text{thf})_2$ , **3**, as a minor product. A preliminary X-ray crystal analysis<sup>†</sup> at  $-80^\circ\text{C}$  has

<sup>†</sup> Crystal data for **3** and **4**: For **3**:  $\text{C}_{86}\text{H}_{16}\text{Bi}_9\text{F}_{65}\text{O}_{22}$ ,  $M = 3788.92$  g mol<sup>-1</sup>, monoclinic space group  $C2/c$  (No. 15),  $a = 65.9(1)$ ,  $b = 15.64(3)$ ,  $c = 27.64(3)$  Å,  $\beta = 109.3(2)^\circ$ ,  $V = 26900(200)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 2.230$  g cm<sup>-3</sup>. Full-matrix least-squares refinement of 293 parameters gave  $R = 0.093$ ,  $R_w = 0.095$  for 4668 unique reflections. The pentafluorophenyl groups were refined as rigid bodies.

For **4**:  $\text{C}_{92}\text{H}_{16}\text{Bi}_9\text{F}_{65}\text{O}_{20}$ ,  $M = 3828.99$  g mol<sup>-1</sup>, primitive space group  $P1$  (No. 2),  $a = 14.626(8)$ ,  $b = 29.461(7)$ ,  $c = 14.12(1)$  Å,  $\alpha = 98.07(4)$ ,  $\beta = 118.08(4)$ ,  $\gamma = 86.34(4)^\circ$ ,  $V = 5313(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.848$  g cm<sup>-3</sup>. Full-matrix least-squares refinement of 800 parameters gave  $R = 0.072$ ,  $R_w = 0.082$  for 8276 unique reflections.

Data were collected at  $-80^\circ\text{C}$  on a Rigaku AFC5 diffractometer with monochromated Mo-K $\alpha$  radiation and corrected for Lorentz polarization and absorption effects. 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.

revealed **3** to be a complex cluster containing nine bismuth atoms, seven oxide ligands, thirteen pentafluorophenoxide ligands and two loosely coordinated thf ligands [with Bi-O(thf) distances of 2.61(5) and 2.77(5) Å]. Significant decay of the crystal in the X-ray beam leads to a crystal structure in which the positions of the lighter atoms are not well defined but clearly present. In addition the thf ligands appear to be somewhat disordered. The structure of **3** is supported by a closely related compound described below.

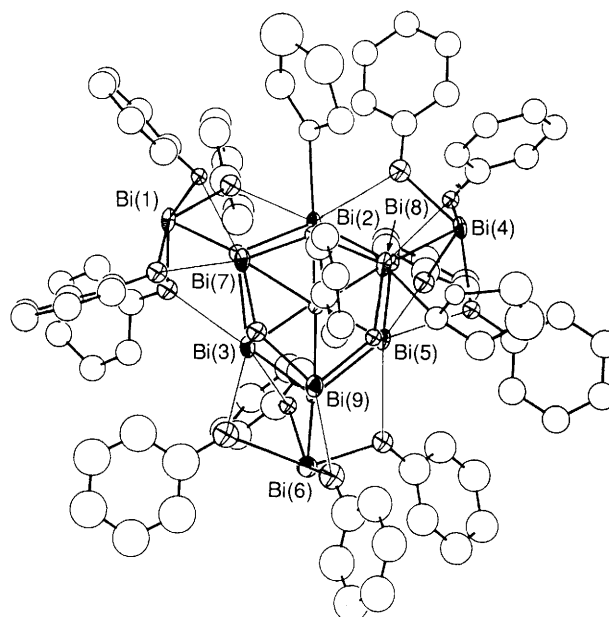


Fig. 1 ORTEP diagram of **3** showing non-hydrogen atoms at 30% probability. Fluorine atoms were omitted for clarity.

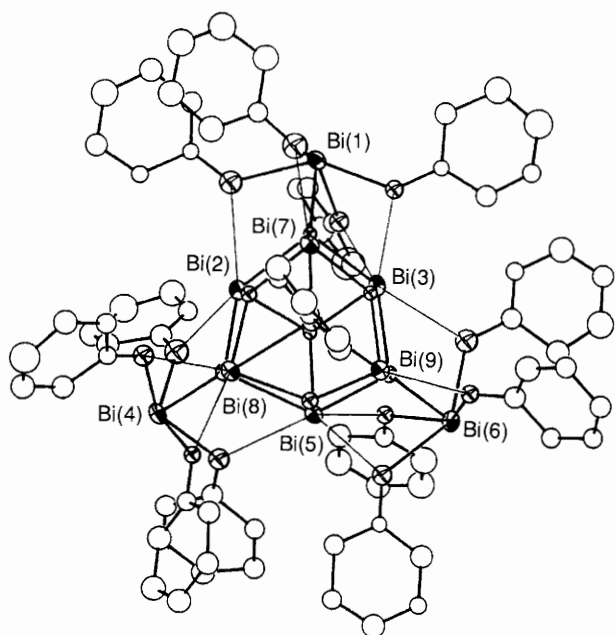


Fig. 2 ORTEP diagram of 4 showing non-hydrogen atoms at 40% probability. Fluorine atoms were omitted for clarity.

The reaction between bismuth trichloride and three equivalents of  $\text{NaOC}_6\text{F}_5$  in thf produces a highly moisture-sensitive, yellow, crystalline compound, which has not yet yielded to characterization. This product is not the bismuth(III) aryloxide dimer 2 mentioned above although analogous reactions between  $\text{NaOR}$  [ $\text{R} = \text{CH}(\text{CF}_3)_2$ , *tert*-butyl] and bismuth trichloride have been used successfully to form  $\text{Bi}(\text{OR})_3^{2a,c}$ . However, brief exposure to air of a toluene solution of this compound yielded a small crop of well formed pale-yellow crystals of 4. An X-ray crystal analysis<sup>†</sup> at  $-80^\circ\text{C}$  has revealed 4 to be analogous to 3 without the two thf ligands. Two non-bonded lattice toluene molecules are also present. Compounds 3 and 4 are likely formed *via* the hydrolysis of a bismuth(III) aryloxide by adventitious water, however, there is growing evidence that oxide ligands can be derived from OR groups.<sup>3</sup>

Compounds 3 and 4, which are the largest structurally characterized bismuth aggregates to date, contain octahedral  $[\text{Bi}_6(\mu_3\text{-O})_7(\mu_3\text{-OC}_6\text{F}_5)]^{3+}$  cores, which are capped on seven of the eight faces with  $\mu_3$ -oxide ligands. The eighth face is asymmetrically capped by  $\mu_3$ -pentafluorophenoxide ligands with two bismuth–oxygen contacts of  $2.52(8)$  Å (avg);<sup>‡</sup> and one very long contact at  $2.76(15)$  Å (avg). The two structures have nearly identical average bond lengths in the core. Comparable core structures are found in basic bismuth nitrate salts:  $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$  and  $[\text{Bi}_6(\text{H}_2\text{O})(\text{NO}_3)_4(\text{OH})_4](\text{NO}_3)_3$ .<sup>4</sup> An overall neutral compound results for compounds 3 and 4 as three of the  $\mu_3$ -oxide ligands act as donor groups to three  $[\text{Bi}(\text{OC}_6\text{F}_5)_4]^-$  groups. The aryloxide ligands on these bismuth atoms show some weaker interactions to nearby bismuth atoms in the  $\text{Bi}_6$  core. Alternatively, the cluster structure can be viewed as a close-packed array of bismuth atoms. Three bismuth atoms of the octahedron and the three bismuth atoms of the appended  $[\text{Bi}(\text{OC}_6\text{F}_5)_4]^-$  groups lie in a plane. The maximum deviation from this plane is  $0.03$  Å for both structures.

There are four distinct bismuth coordination geometries in clusters 3 and 4. The bismuths of the appended  $[\text{Bi}(\text{OC}_6\text{F}_5)_4]^-$

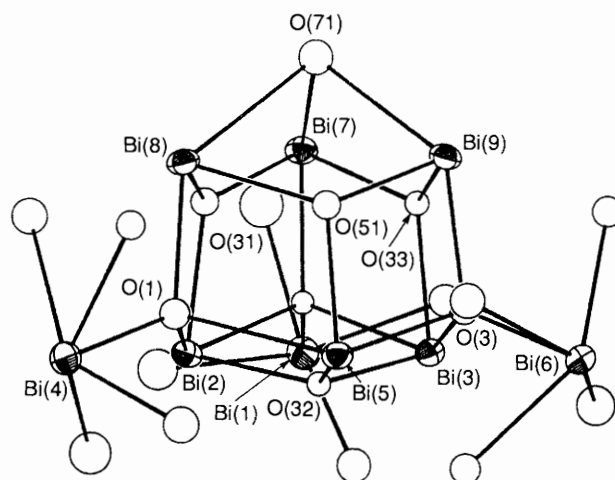


Fig. 3 ORTEP diagram of 4 omitting the pentafluorophenyl rings and the lattice toluene for clarity

groups [Bi(1), Bi(4) and Bi(6)] are ligated by four alkoxide ligands with distances of  $2.35(8)$  (avg) for 3 and  $2.32(10)$  Å (avg) for 4. The distances of the bismuth to the oxygens of the cluster core are shorter at  $2.15(7)$  (avg) for 3 and  $2.10(3)$  Å (avg) for 4. The coordination geometry can be loosely described as pseudo-square pyramidal with the equatorial oxygens bent toward the apical oxygen. The bismuth atoms of the core have very irregular geometries. Each has four contacts to the  $\mu_3$ -oxygen atoms that cap the octahedral faces of the core. Some bridging interactions are observed between the alkoxide ligands of the  $[\text{Bi}(\text{OC}_6\text{F}_5)_4]^-$  groups and the bismuth atoms of the cluster core. These interactions are not regular and in each compound two bismuth atoms have one close contact,  $2.62(8)$  Å (avg), two have two contacts ( $2.41$ – $2.84$  Å) and two have three contacts ( $2.49$ – $2.86$  Å).

The bismuth–oxygen bond distances in these cluster compounds are comparable with those found in  $\alpha\text{-Bi}_2\text{O}_3$ ,<sup>5</sup> which is made up of two kinds of bismuth centres. Each has five neighbours at a distance of  $2.13$ – $2.6$  Å and either one more at  $2.8$  or two more at  $3.3$  and  $3.4$  Å.

The formation of mixed metal alkoxides is attractive in order to achieve more intimate mixing in sol–gel or vapour deposition syntheses. A central  $[\text{Bi}_6\text{O}_8]^{2+}$  core may be a useful synthon for production of complexes onto which other  $[\text{M}(\text{OR})_x]^-$  functionalities, such as  $\text{Cu}(\text{OR})_3^-$ , may be attached. Attempts to isolate this core moiety are in progress.

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<sup>‡</sup> Esds of average values are calculated with the scatter formula, eqn. (1).

$$\sigma = \left[ \frac{\sum_{i=1}^{i=N} (d_i - d)^2}{N-1} \right]^{1/2} \quad (1)$$