

# Bismuth Pyrostannate, $\text{Bi}_2\text{Sn}_2\text{O}_7$ , from the First Structurally Characterized Heterobimetallic Bi:Sn Alkoxides

Philip C. Andrews,\* Peter C. Junk, Iryna Nuzhnaya, and Dominique T. Thielemann

School of Chemistry, Monash University, Clayton, Melbourne, Vic. 3800, Australia

**S** Supporting Information

**ABSTRACT:** The first heterobimetallic Bi:Sn alkoxide complexes  $[\text{Bi}_2\text{SnO}(\text{OCH}(\text{CF}_3)_2)_5(\text{O}^t\text{Bu})_3(\text{THF})]$  (**1**) and  $[\text{BiSnO}(\text{OCH}(\text{CF}_3)_2)_3(\text{O}^t\text{Bu})_2]_2$  (**2**) are described. The complexes were obtained through mixing and heating equimolar quantities of the component alkoxides,  $\text{Bi}(\text{OCH}(\text{CF}_3)_2)_3$  and  $\text{Sn}(\text{O}^t\text{Bu})_4$ , under solvent-free conditions (**1**) and in THF (**2**). The solid-state structures were determined by single crystal X-ray diffraction showing ligand redistribution from Bi(III) to Sn(IV) in the two molecular species. Compound **2** behaves as a single-source precursor for the thermolytic formation of bismuth pyrostannate,  $\text{Bi}_2\text{Sn}_2\text{O}_7$ .

Tin and bismuth alkoxides are important precursors in the formation of their respective oxide films,  $\text{SnO}_2$  and  $\text{Bi}_2\text{O}_3$ , and their incorporation in ternary materials.<sup>1</sup> While the homometallic oxides have chemical and physical features that make them important in modern materials chemistry,<sup>2,3</sup> much recent interest has come to focus on the properties and utility of heterometallic systems.<sup>4</sup> These systems allow for greater variation in the physical, structural, electronic, and optical properties of the materials and can accommodate greater specificity in their application. Bismuth pyrostannate  $\text{Bi}_2\text{Sn}_2\text{O}_7$  is a desirable ternary oxide<sup>5</sup> showing good catalytic activity and utility in a wide array of organic transformations and can act as a selective CO-sensing device.

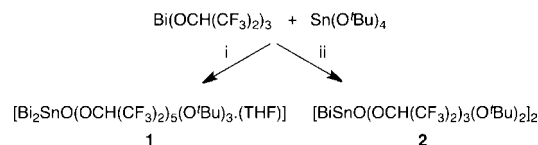
While the chemistry of  $\text{Sn}(\text{OR})_4$  species and their application in the deposition of thin films is now relatively well established,<sup>6</sup> that of homometallic  $\text{Bi}(\text{OR})_3$  is somewhat more limited, mostly stemming from difficulties in synthesis, solubility, and volatility.<sup>3,7,8</sup> These difficulties are amplified in the exploration of bismuth-containing heterobimetallic systems.<sup>9</sup> Heterobimetallic single-source precursors have been long touted as being ideal for the controlled formation of ternary oxide materials. However, the lack of success in their formation and isolation means that the predominant method for oxide formation remains the premixing of two discrete homometallic species, with accompanying problems of solubility, stoichiometry, and mismatching of reactivity and decomposition profiles.

Despite alkoxide-based heterobimetallic complexes being identified and targeted as the best and most flexible systems for oxide formation under mild conditions,<sup>10,11</sup> the molecular compounds remain elusive. Very few heterobimetallic bismuth alkoxides have been reported in the literature, and even less characterized in the solid state.<sup>3,12,13</sup> Of these, most involve the

alkali and alkaline earth metals.<sup>3,14–17</sup> To date, there is only one example in the literature of a complex containing bismuth(III) with a second different p-block metal, namely,  $[\text{Bi}\{\text{Al}(\text{O}^i\text{Pr})_4\}_2(\text{O}^i\text{Pr})]$ . However, while the composition is reported, the solid-state structure has not been established.<sup>18</sup> The majority of heterobimetallic complexes are composed of carboxylates or diketonates as O-bound ligands and contain d-block metals alongside bismuth.<sup>9</sup>

Herein, we report the synthesis, structural characterization, and thermolysis of two heterobimetallic Bi:Sn alkoxide complexes:  $[\text{Bi}_2\text{SnO}(\text{OCH}(\text{CF}_3)_2)_5(\text{O}^t\text{Bu})_3(\text{THF})]$  (**1**) and  $[\text{BiSnO}(\text{OCH}(\text{CF}_3)_2)_3(\text{O}^t\text{Bu})_2]_2$  (**2**), both derived from the equimolar combination of the component metal alkoxides,  $\text{Bi}(\text{OCH}(\text{CF}_3)_2)_3$  and  $\text{Sn}(\text{O}^t\text{Bu})_4$  (Scheme 1). The two complexes, however, were synthesized using two different synthetic routes.

**Scheme 1**<sup>a</sup>



<sup>a</sup>Reaction conditions: (i) solvent-free, 60 °C,  $\text{N}_2(\text{g})$ , 30 min, THF and toluene extraction; (ii) THF, 60 °C,  $\text{N}_2(\text{g})$ , 30 min, hexane and toluene extraction.

Compound **1** was obtained from the treatment of  $\text{Bi}(\text{OCH}(\text{CF}_3)_2)_3$  (mp 52 °C) with  $\text{Sn}(\text{O}^t\text{Bu})_4$  (mp 42 °C) under solvent-free conditions, heating to 60 °C under  $\text{N}_2$  for 30 min. This produced a white solid from a molten mixture, which was washed with hexane to remove unreacted material. Ultimate extraction of the solid with hot toluene gave a clear yellow solution. Colorless crystals of **1** were readily obtained on allowing the solution to cool slowly to room temperature. The origin of the preference for a Bi:Sn ratio of 2:1 is not yet known but may be due to differences in ligand lability and the ease of  $\text{M}-\text{OR}$  decomposition and/or dissociation.

Compound **2** was synthesized in a more conventional way, combining THF solutions of the Bi and Sn alkoxide precursors and heating to 60 °C for 30 min. Removal of THF under vacuum conditions gave a viscous yellow oil which was washed with *n*-hexane and taken up in hot toluene. As with **1**, single

Received: May 31, 2011

Published: January 4, 2012

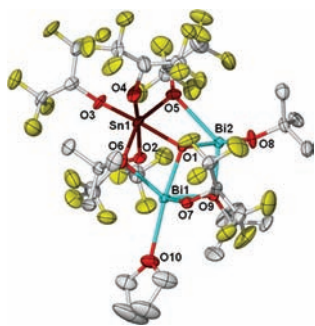
crystals of **2** were obtained by allowing the solution to cool to room temperature.

The isolated yields of crystals of **1** and **2** were 26% and 42%, respectively. Both compounds have relatively low melting points; **1** melts in the range 114–117 °C and **2** from 105 to 107 °C. Single crystal X-ray diffraction studies show that **1** is a heteroleptic trinuclear system of formula  $[\text{Bi}_2\text{SnO}(\text{OCH}(\text{CF}_3)_2)_5(\text{O}^t\text{Bu})_3(\text{THF})]$ , containing one coordinating THF molecule, while **2** is a binuclear complex  $[\text{BiSnO}(\text{OCH}(\text{CF}_3)_2)_3(\text{O}^t\text{Bu})_2]_2 \cdot \text{C}_7\text{H}_8$ , accommodating one toluene molecule in the crystal lattice. The elemental analysis of **1** is consistent with the crystal structure, while for **2** it is consistent with the loss of the noncoordinating toluene molecule. CCDC 827443 and 827444 contain the supplementary crystallographic data for this paper. These data (excluding structure factors) can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

A significant problem in forming isolable heterobimetallic alkoxides is the high lability of the ligands, combined with the different electronic and physical properties of the metals. Solution-state NMR spectroscopic studies on **1** and **2** conducted in THF- $d_8$  and  $\text{C}_6\text{D}_6$  exemplify this problem. The spectra show evidence of the compounds undergoing dynamic rearrangement in solution, forming species of differing nuclearity, substitution, and thus composition. This is also evident in the single crystal X-ray structure of **2**, which displays a dual site occupancy by  $\text{O}^t\text{Bu}$  and  $\text{OCH}(\text{CF}_3)_2$  at a single bridging position (see below). For both **1** and **2**, the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra at room temperature show numerous resonances corresponding to the  $\text{C}(\text{CH}_3)_3$  and  $\text{OCH}(\text{CF}_3)_2$  groups, though the spectra in THF- $d_8$  show greater signal averaging than those obtained in  $\text{C}_6\text{D}_6$  (these data are provided in the Supporting Information). The  $^{19}\text{F}$  NMR spectrum for **1** has a single dominant doublet at  $\delta -74.72$  and for **2** at  $\delta -75.85$ . The  $^{119}\text{Sn}$  NMR spectra revealed one singlet for each of the title compounds, at  $\delta -249.3$  for **1** and  $\delta -701.4$  for **2**.

The NMR spectra, coupled with elemental analyses, indicate that compounds of composition consistent with **1** and **2** are formed reproducibly.

Compound **1** crystallizes in space group  $P2_1/n$  with the whole molecule comprising the asymmetric unit (Figure 1).



**Figure 1.** Crystal structure of trinuclear complex  $[\text{Bi}_2\text{SnO}(\text{OCH}(\text{CF}_3)_2)_5(\text{O}^t\text{Bu})_3(\text{THF})]$  (**1**). Ellipsoids are shown at 50% probability. All hydrogen atoms are omitted for clarity.

The asymmetric unit consists of a trinuclear metal core incorporating a hexa-coordinate Sn atom, and penta- and tetra-coordinate Bi atoms, Bi(1) and Bi(2), respectively. The intermetallic distances are  $\text{Sn}(1)\cdots\text{Bi}(1) = 3.304 \text{ \AA}$ ,  $\text{Sn}(1)\cdots\text{Bi}(2) = 3.516 \text{ \AA}$ , and  $\text{Bi}(1)\cdots\text{Bi}(2) = 3.513 \text{ \AA}$ . These

three metal atoms are bridged around the perimeter by three alkoxy groups: one  $\text{OCH}(\text{CF}_3)_2$  group bridges Sn and Bi atoms with bond distances of  $\text{Sn}(1)\text{--O}(5) = 2.074(7) \text{ \AA}$  and  $\text{Bi}(2)\text{--O}(5) = 2.662(7) \text{ \AA}$ , and one  $\text{O}^t\text{Bu}$  group bridges Sn and Bi atoms with bond distances of  $\text{Sn}(1)\text{--O}(6) = 2.062(7) \text{ \AA}$  and  $\text{Bi}\text{--O}(6) = 2.337(6) \text{ \AA}$ . A second  $\text{O}^t\text{Bu}$  group straddles the two Bi atoms with one short bond,  $\text{Bi}(2)\text{--O}(9) = 2.185(6) \text{ \AA}$ , and one longer bond,  $\text{Bi}(1)\text{--O}(9) = 2.344(6) \text{ \AA}$ . The Sn and two Bi atoms are linked by a central asymmetrically bonded  $\mu_3\text{-O}$  atom with distances of  $\text{Sn}(1)\text{--O}(1) = 2.089(6) \text{ \AA}$ ,  $\text{Bi}(1)\text{--O}(1) = 2.176(5) \text{ \AA}$ , and  $\text{Bi}(2)\text{--O}(1) = 2.092(6) \text{ \AA}$ .

The coordination environment around Sn(1) is distorted octahedral with bond angles in the range of  $76.5(2)\text{--}169.1(3)^\circ$ . In addition to the two bridging alkoxy groups, the Sn atom has three terminal coordinated  $\text{OCH}(\text{CF}_3)_2$  groups with an average Sn–O bond distance of 2.08 Å, which is more consistent with distances observed in Sn(II) complexes, e.g.,  $[\text{Sn}(\text{OCH}(\text{CF}_3)_2)_2(\text{HNMe}_2)]$ .<sup>19</sup>

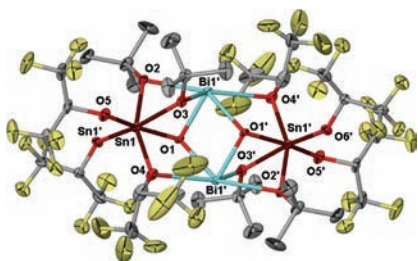
The two Bi atoms have distinctive coordination environments. The four-coordinate Bi(2) atom has distorted trigonal bipyramidal geometry, with bond angles in the range of  $64.8(2)\text{--}130.6(2)^\circ$ . In addition to the two bridging alkoxy groups and the central O atom, it coordinates to a terminal  $\text{O}^t\text{Bu}$  ligand at a bond distance of  $\text{Bi}(2)\text{--O}(8) = 2.037(6) \text{ \AA}$ .

The penta-coordinate Bi(1) atom has a distorted octahedral geometry with bond angles in the range of  $69.3(2)\text{--}166.8(2)^\circ$ . In addition to the two definite bridging alkoxy ligands and the bond with the central O atom, Bi(1) bonds with a terminal  $\text{OCH}(\text{CF}_3)_2$  ligand at a distance of  $\text{Bi}(1)\text{--O}(7) = 2.092(6) \text{ \AA}$ , and with the single terminal THF molecule,  $\text{Bi}(1)\text{--O}(10) = 2.710(7) \text{ \AA}$ . It expands its coordination environment to six if the longer, weaker interaction between Bi(1) and O(2), 3.263 Å, is also taken into account.

The observed bridging and terminal Bi–O bond distances are largely consistent with those observed in related homometallic bismuth compounds.<sup>20,21</sup> For example, in  $[\text{Bi}_2(\mu_3\text{-O})(\text{OCH}(\text{CF}_3)_2)_2(\mu\text{-OCH}(\text{CF}_3)_2)_2(\text{THF})_2]$ ,<sup>21</sup> the terminal Bi– $\text{OCH}(\text{CF}_3)_2$  distances are 2.082(6) and 2.133(6) Å, while the bridging ligands show a more varied bonding pattern with distances ranging from 2.219(7)–2.702(7) Å. The average distance from the three Bi atoms in this complex to the central  $\mu_3\text{-O}$  is 2.14 Å.

Compound **2** crystallizes in the triclinic crystal system  $P\bar{1}$  with two independent half molecules (**2A** and **2B**) in the asymmetric cell. The central planar  $\text{Bi}_2\text{O}_2$  parallelogram in each molecule resides on an inversion center. While the atoms in one half-molecule (**A**) could be satisfactorily refined, the other half-molecule (**B**) suffers from significant disorder in both its  $\text{OCH}(\text{CF}_3)_2$  groups. This is attributed to high thermal motion and in having one of the metal bridging sites occupied 50:50 by  $\text{OCH}(\text{CF}_3)_2$  and  $\text{O}^t\text{Bu}$  groups. The remaining bridging  $\text{O}^t\text{Bu}$  group shows no disorder or partial occupancy, and the structure of **2A** is presented in Figure 2.

The bond lengths in the central  $\text{Bi}_2\text{O}_2$  ring are  $\text{Bi}(1)\text{--O}(1) = 2.111(8) \text{ \AA}$  and  $\text{Bi}(1)\text{--O}(1') = 2.190(7) \text{ \AA}$ . The Sn atoms then adopt a *trans* orientation relative to the ring, with each emanating from separate ring O atoms at an angle of  $119.6(3)^\circ$  and bonding at a distance of  $\text{Sn}(1)\text{--O}(1) = 2.100(7) \text{ \AA}$ . One bridging and two terminal  $\text{OCH}(\text{CF}_3)_2$  groups, and two bridging  $\text{O}^t\text{Bu}$  groups, contribute to a distorted octahedral coordination environment around the Sn atom. The terminal bond distances,  $\text{Sn}(1)\text{--O}(5)$  and  $\text{Sn}(1)\text{--O}(6)$ , are essentially identical at 1.988(8) and 1.994(8) Å, respectively. The bridging

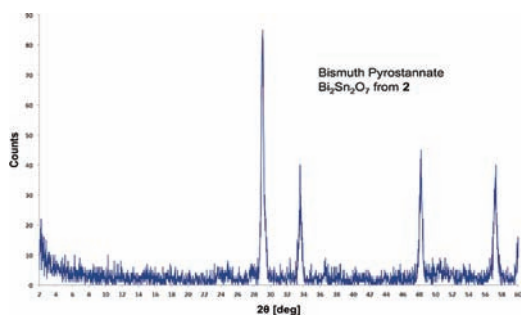


**Figure 2.** Crystal structure of  $[\text{BiSnO}(\text{OCH}(\text{CF}_3)_2)_3(\text{O}^t\text{Bu})_2]_2 \cdot \text{C}_7\text{H}_8$ , **2A**. Ellipsoids are shown at 30% probability. All hydrogen atoms and the lattice toluene molecule are omitted for clarity.

$\text{OCH}(\text{CF}_3)_2$  group forms a much shorter bond to tin,  $\text{Sn}(1)-\text{O}(4) = 2.052(8) \text{ \AA}$ , than it does to bismuth,  $\text{Bi}(1')-\text{O}(4) = 2.813 \text{ \AA}$ . One of the bridging  $\text{O}^t\text{Bu}$  groups forms a shorter bond with tin than with bismuth,  $\text{Sn}(1)-\text{O}(2) = 2.075(9)$  and  $\text{Bi}(1)-\text{O}(2) = 2.454(8) \text{ \AA}$ , while the opposite is the case for the other,  $\text{Sn}(1)-\text{O}(3) = 2.207(8)$  and  $\text{Bi}(1)-\text{O}(3) = 2.157(8) \text{ \AA}$ . Most likely, this is due to steric effects. If the stereochemically active lone pair on  $\text{Bi}(1)$  is included in the coordination environment, then the Bi center adopts a highly distorted octahedral arrangement. There are four acute angles involving  $\text{Bi}(1)$  and  $\text{O}(1-3)$  ranging from  $62.2(3)$  to  $75.8(3)^\circ$  and a single obtuse angle of  $147.8(3)^\circ$  for  $\text{O}(2)-\text{Bi}(1)-\text{O}(2)$ .

Thermal decomposition profiles of **1** and **2** were studied via thermogravimetric analysis (TGA). Unfortunately, the final weight-percent values did not allow for an unambiguous assignment to a certain oxide or oxyfluoride species (see the Supporting Information) though energy dispersive spectroscopy (EDS) experiments on the residues were consistent with the Bi:Sn ratios of **1** and **2**.

As such, microcrystalline samples of **1** and **2** were combusted and annealed at  $700^\circ\text{C}$  for 24 h and the thermolytic decomposition products analyzed with PXRD and XDS. Both compounds show preferential formation of the ternary oxide



**Figure 3.** PXRD profile of  $\text{Bi}_2\text{Sn}_2\text{O}_7$  obtained from the pyrolysis of **2** in air.

$\text{Bi}_2\text{Sn}_2\text{O}_7$  (Figure 3).<sup>5</sup> There is no evidence of oxyfluoride formation.

For **1**, the XRD pattern shows additional and coincident reflections for  $\text{Bi}_2\text{O}_3$ , reflecting the stoichiometric 2:1 ratio of Bi and Sn in **1** (see Supporting Information). Compound **2** gives exclusively  $\text{Bi}_2\text{Sn}_2\text{O}_7$ , reflecting the 1:1 Bi/Sn ratio, and thereby acts as an effective single source precursor to bismuth pyrostannate by thermal decomposition.

The mechanism of formation of both **1** and **2** involves a ligand transfer process, in which the anionic hexafluoroalkoxide

groups move away from the Bi(III) centers to the more electropositive Sn(IV) centers. The concomitant formation of the oxo-species, and by inference the mechanism of formation of the final ternary oxide species, was investigated using GC-MS (see Supporting Information). The alkoxides were mixed, dried *in vacuo*, and heated under an atmosphere of dry argon gas to  $100^\circ\text{C}$  for 1 h. Head-space GC-MS analysis of the volatile components showed them to be unambiguously *iso*-butylene,  $^t\text{BuOH}$ , and  $(\text{CF}_3)_2\text{CHOH}$ . This is consistent with known decomposition pathways of highly branched metal alkoxides.<sup>22</sup>

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Syntheses, analyses, and crystallographic data, including CIFs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### ✉ Corresponding Author

\*Ph.: +61 3 9905 5509. Fax: +61 3 99054597. E-mail: phil.andrews@monash.edu.

## ■ ACKNOWLEDGMENTS

We thank the Australian Research Council, Monash University, and Smartprint CRC for financial support.

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