The Synthesis and Materials Chemistry of Bismuth Tris-(di-i-propylcarbamate) : Deposition of Photoactive Bi₂O₃ Thin Films

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Abstract

The bismuth carbamate Bi(O₂CNPr₂)₃, a tetramer in the solid-state, has been synthesised and used to deposit mixtures of bismuth oxides by aerosol-assisted chemical vapour deposition (AACVD). The nature of the deposited oxide is a function of both temperature and run-time. Initially, δ-Bi₂O₃ is deposited, over which grows a thick layer of β-Bi₂O₃ nanowires, the latter having an increasing degree of preferred orientation at higher deposition temperatures. The photocatalytic activity of a thin film of δ-Bi₂O₃ for the degradation of methylene blue dye was found to be similar to that of a commercial TiO₂ film on glass, while the film overcoated with β-Bi₂O₃ nanowires was less active. Exposure of Bi(O₂CNPr₂)₃ to controlled amounts of moist air affords the novel oxo-cluster Bi₈(O)₆(O₂CNPr₂)₁₂, whose structure has also been determined.

Keywords: Bismuth, carbamate, oxide, oxo-cluster, thin film, photocatalyst
Introduction

Carbamates (R₂NCO₂⁻) are an interesting class of ligand which form a link between carboxylates (RCO₂⁻) and dithiocarbamates (R₂NCS₂⁻). They have been widely studied as metal complexes across most of the Periodic Table,¹ though surprisingly only one brief report has appeared concerning bismuth.² Beyond the structural interest, carbamates (or isomers thereof) offer an alternative ligand for the formation of potentially volatile precursors for chemical vapour deposition (CVD),³ ⁴ and in this regard the two substituents on nitrogen offer additional opportunities for steric crowding, in comparison with, for example, carboxylates. Bismuth carbamates are, therefore, possible precursors for Bi₂O₃, a material exploited either alone⁵ or, more significantly, as a component of more complex materials such as Bi₂Sn₂O₇ (catalyst, CO sensor),⁶ ⁷ BiFeO₃ (a multiferroic compound),⁸ Bi₄ YT₃O₁₂ and SrBi₂Ta₃O₉ (ferroelectric perovskites)⁹ ¹⁰ and Bi₂Sr₂CaCu₂O₈ (high temperature superconductor).¹¹ Existing CVD precursors for bismuth oxides include Bi₃,¹²⁻¹₈ Bi(NO₃)₃,¹⁹ BiPh₃²⁰⁻²₂ and related bismuth aryls²³ and alkyls,²⁴ β-diketonates such as Bi(thd)₃ (thd = tetramethylheptanegdione),²³ ²⁵ ²⁶ and both simple and functionalised alkoxides,²⁷⁻²⁹ all summarised in refs. 5 and 28. However, of these only the three alkoxides²⁷⁻²⁹ are single-source precursors (SSPs), the remainder requiring a co-reactant, usually O₂.

In this paper we report the first structural characterisation of a bismuth carbamate, and its controlled hydrolysis to an unusual Bi₈-oxo cluster, along with use of the carbamate as a CVD precursor for photoactive Bi₂O₃ thin films.

Experimental Section

General Procedures: All operations were performed under an atmosphere of dry argon using standard Schlenk line and glovebox techniques. Hexanes were dried using a commercially available solvent purification system (Innovative Technology Inc., MA, USA) and degassed under argon prior to use. Tetrahydrofuran (THF) was dried by refluxing over potassium before isolating by distillation and degassing under argon prior to use. Deuterated benzene (C₆D₆) and deuterated chloroform (CDCl₃) NMR solvents were purchased from Fluorochem, UK, and dried by refluxing over potassium and over 4 Å molecular sieves respectively, before isolating via vacuum distillation. All dry solvents were stored under
argon in Young’s ampoules over 4 Å molecular sieves. BiCl$_3$ and 2M solution of LiNPr$_2^+$ were purchased from commercial sources and used as received. Bi(NPr$_2^+$)$_3$ was prepared by a literature procedure.$^{30}$

Melting points were determined utilising a Stuart SMP10 Melting Point Apparatus. Elemental analyses were performed externally by London Metropolitan University Elemental Analysis Service, UK. Solution $^1$H and $^{13}$C($^1$H) NMR spectra were recorded with a Bruker Avance 300 spectrometer at ambient temperature (25 °C). $^1$H and $^{13}$C NMR chemical shifts are referenced internally to residual non-deuterated solvent resonances. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. The following abbreviations are used: d (doublet), m (multiplet) and br (broad).

**Synthesis of Bi(O$_2$CNPr$_2$)$_3$ (1).** Dry CO$_2$ was slowly bubbled through a stirred solution of Bi(NPr$_2^+$)$_3$ (0.510 g, 1 mmol) in hexanes (15 mL) for 30 minutes. Crystallisation from the reaction solution at -28 °C yielded the desired product as small colourless crystals. Yield = 0.526 g, 83%.

Alternatively, the same compound can be prepared in a one-pot synthesis, as follows. A stirred suspension of BiCl$_3$ (8.514 g, 27 mmol) in THF (100 mL) was slowly treated at -78 °C with a 2M THF/n-heptane/ethylbenzene solution of LiNPr$_2^+$ (42.0 mL, 84 mmol). The reaction solution was slowly allowed to warm to ambient temperature and stirred for 4 h, before volatiles were removed *in vacuo*. To the residue, hexanes (150 mL) were added and the resultant solution filtered through Celite. Dry CO$_2$ was then slowly bubbled through the solution for 1 h, with subsequent crystallisation from the reaction solution at -28 °C yielding the desired product as colourless crystals. Yield: 11.96 g, 69%. m.p. 91 - 92 °C. Analysis, found (calculated for C$_{21}$H$_{42}$BiN$_3$O$_6$): C 39.46 (39.31), H 6.52 (6.60), N 6.68 (6.55)%. $^1$H NMR (300 MHz, C$_6$D$_6$): δ$_H$ 3.92 (br m, 1H, CHCH$_3$), 1.28 (d, 6H, CHC$_3$, $^3$J$_{CHCH3}$ 6.6). $^{13}$C($^1$H) NMR (75.5 MHz, C$_6$D$_6$): δ$_C$ 163.6 (NCO$_2$), 45.9 (CH), 21.2 (CH$_3$).

**Synthesis of Bi$_8$(O)$_6$(O$_2$CNPr$_2$)$_{12}$ (2).** A hexanes solution containing 1 was prepared as described above before volatiles were subsequently removed *in vacuo*. The resultant residue was dissolved in THF (15 mL) and the solution was then filtered. Compound 2 was obtained as colourless crystals by crystallisation from this reaction solution upon partial exposure to the ambient atmosphere for 72 h. Yield: 0.09 g, 21%. m.p. 204 - 208 °C (dec.). Analysis, found (calculated for C$_{84}$H$_{168}$Bi$_8$N$_{12}$O$_{30}$): C 28.81 (28.84), H 4.75 (4.84),
N 4.77 (4.80)%. $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H$ 4.33-3.60 (br m, 3H, CH$_2$), 2.98-2.83 (m, 1H, CH$_3$), 1.23 (d, 6H, CHCH$_3$, $^3$J$_{CHCH_3}$ 6.3), 1.19-1.07 (m, 12H, CHCH$_3$), 1.04 (d, 6H, CHCH$_3$, $^3$J$_{CHCH_3}$ 6.2). $^{13}$C($^1$H)

NMR (75.5 MHz, CDCl$_3$): $\delta_C$ 162.9, 161.8 (NCO), 45.3 (CH), 21.2, 21.1, 21.0 (CH$_3$).

DOSY NMR Procedure:

Diffusion experiments were performed for 1 M and saturated solutions of 1 in dried d$_8$-toluene and were recorded at 298 K and 353 K on a Bruker Avance 400 spectrometer operating at 400.13 MHz for $^1$H. Experiments were performed using a double stimulated echo pulse sequence to allow for convection compensation, with $\Delta$ of 50 ms and $\delta$ of 2 ms. Gradient strengths were incremented linearly, in eight steps, from 1.74 to 33.14 Gcm$^{-1}$, with 16 scans recorded at each gradient strength. Diffusion coefficients were calculated using Bruker’s inbuilt T1/T2 software. The hydrodynamic radius ($r$) of 1 was calculated using the Stokes-Einstein equation:

$$r = \frac{k_BT}{6\pi\eta D}$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature, $\eta$ is the viscosity of the solution and $D$ is the diffusion coefficient.

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in Table 1. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Structure solution followed by full-matrix least squares refinement was performed using the WinGX-1.70 suite of programmes. Corrections for absorption (multi-scan) were made in both cases. The asymmetric unit of 1 consists of one quarter of the tetrameric complex and a co-crystallised solvent molecule at half occupancy. This latter has been modelled as pentane, though symmetry places two such molecules in close proximity. It is likely that the solvent present is a mixture of hexane isomers (see the synthetic protocol), though we have made no further effort to model this aspect of the structure given its relative unimportance. Bond lengths and angles in the solvent molecule have
been geometrically fixed and C(35) is refined isotropically. 2: The asymmetric unit contains three THF molecules (6 per Bi₈ cluster), one of which is disordered over two sites in a 87:13 ratio.

**Materials Chemistry**

Thermogravimetric analyses (TGA) were performed either at SAFC HiTech, Bromborough, UK, using a Shimadzu TGA-51 Thermogravimetric Analyzer (1), or at Bath using a TA Instruments Q500 TGA instrument (2). Data points were collected every second at a ramp rate of 10 °C min⁻¹ in a flowing (90 mL min⁻¹) N₂ stream.

 Film depositions were carried out at atmospheric pressure in a cold-wall Electrogas reactor containing a graphite heating block on which the substrate is situated. The precursor was injected as a 0.05 M hexanes solution (20 mL) into a glass flask sitting in an ultrasonic nebulizer, located just before the reactor chamber. Prior to injecting the precursor, the chamber was loaded with the substrate and heated under a flow of preheated nitrogen (0.8 L/min, 120 °C) to the required temperature before allowing it to equilibrate for at least 30 min. The precursor was then injected and the nebulizer started to begin the deposition. Films were deposited on glass substrates at 300 °C for run times of 10 min (R1) and 40 min (R2), at 375 °C for 40 min (R3) and at 450 °C for 40 min (R4). After each deposition, the films were allowed to cool slowly to ambient temperature under a flow of nitrogen. The glass substrates (glass microscope slides) were cleaned via sonication in Piranha solution, rinsed with deionized water and dried under a flow of N₂ prior to loading into the chamber.

**Photocatalysis studies**

The photocatalytic activities of the δ- and β-Bi₂O₃ films were evaluated by the decolorization of methylene blue (MB). A 200 W HMI HR lamp (AM 1.5, 1 Sun, 735 Wm⁻²) was used as a light source to provide broad wavelength solar irradiation. The experiments were performed under ambient temperature as follows: In each run, the photoactive film (2.5 cm²) was placed in a glass vessel and submerged in 10ml of MB solution (1x10⁻⁵ mol L⁻¹). Before illumination, the solution was stirred for 30 min in the dark to equilibrate adsorption-desorption of MB and photocatalyst. The solution was then stirred and exposed to
solar irradiation. The concentration of the MB was monitored by measurement of the absorbance at 665 nm during the photodegradation process using a Varian Cary 50 UV-Visible spectrophotometer.
Table 1. Crystal data and structure refinement for 1 and 2

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<th>Identification code</th>
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<th>2</th>
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<td>16.1210(2)</td>
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**Results and Discussion**

**Synthesis and Structural Chemistry**

The homoleptic bismuth carbamate Bi(O_2CNPr'_{2})_3 (1) was synthesised by the insertion of CO_2 into the Bi-N bond of Bi(NPr'_{2})_3. On bubbling dry CO_2 through a green solution of Bi(NPr'_{2})_3 in hexanes, there is
a colour change to pale yellow over a period of ca. 15 mins. Alternatively, the synthesis is also viable in "one pot", by mixing BiCl₃, LiNPrᵢ₂ and bubbling CO₂ through the mixture without isolation of the Bi(NPrᵢ₂)₃ intermediate. The NMR of 1 is unexceptional, showing the expected doublet / septet pattern for the i-Pr groups in the ¹H NMR and three resonances in the ¹³C NMR (19.8, 44.4, 162.2 ppm), the most diagnostic of which is the latter signifying the formation of the sp² NCO₂ centre.

Compound 1 is moderately air-sensitive and controlled exposure to moist air (by allowing a concentrated solution of 1 to be exposed to the atmosphere over 2 days) leads to the crystallization of the oxo-cluster Bi₈(O)₆(O₂CNPrᵢ₂)₁₂ (2).

\[
\text{Bi(NPrᵢ₂)₃} \xrightarrow{\text{CO₂}} \text{Bi(O₂CNPrᵢ₂)₃} \xrightarrow{\text{moist air}} \text{Bi₈(O)₆(O₂CNPrᵢ₂)₁₂ (2)}
\]

The ¹H NMR spectrum of 2 is complex, but shows that there are two distinct CH and three distinct CH₃ environments which persist in solution arising from restricted rotation about the HC-CH₃ bonds of the peripheral i-Pr groups.
Figure 1. The asymmetric unit of 1 showing the labelling scheme used; thermal ellipsoids are at the 40% probability level. The co-crystallised, disordered solvent molecule, modelled as pentane, has been omitted for clarity. Selected metrical data: Bi-O(1) 2.217(2), Bi-O(2) 2.681(2), Bi-O(3) 2.227(2), Bi-O(4) 2.553(2), Bi-O(5) 2.232(2), Bi-O(6') 2.440(2), Bi-O2'' 2.813(2) Å.

The structure of 1 is shown in Figure 1, along with some selected bond length data. Each bismuth is bonded to two chelating carbamate ligands while the remaining ligand bridges two metal centres. This leads to an overall tetrameric species (Figure 2a), involving a non-planar sixteen-membered \((\text{BiOCO})_4\) ring; the overall shape of the tetramer is that of a box with the lid removed (Figure 2b). The geometry at bismuth can be described as pentagonal bipyramidal, with the two Bi-O bonds associated with the bridging carbamate \([\text{Bi-O}(5) 2.232(2), \text{Bi-O}(6') 2.440(2) \text{ Å}]\) occupying the axial sites and the bonds to the chelating carbamates, including two of the weaker interactions \([\text{Bi-O}(2) 2.681(2), \text{Bi-O}(4) 2.553(2) \text{ Å}]\), along with a void occupied by the lone pair, making up the equatorial girdle. The geometry is, however, severely distorted, with additional long contacts which merit discussion. Firstly, an oxygen of one chelating ligand forms long contacts with the symmetry-related metals either side \([\text{O}(2)\ldots\text{Bi}^+ 2.813(2); \text{O}(2)\ldots\text{Bi}''' 3.293(2) \text{ Å}]\), of which only the shorter is shown in Fig. 2a. There is a further long, chelating contact between bridging O(6) and bismuth \([3.207(2) \text{ Å}]\) but the orientation of the atoms makes this interaction marginal at best; such an interaction, but at 3.27 Å, has been noted in \(\text{Bi(O}_2\text{CBu}_3)^3\).\(^{32}\) Indeed, the structure 1 is comparable to that reported for \(\text{Bi(O}_2\text{CBu}_3)^3\) in that it too exists as cyclic tetrameric units, with two terminal carboxylate ligands and one bridging carboxylate ligand per bismuth centre. For comparison, in the carboxylate the oxygen which protrudes into the centre of the "box" is at 2.87 and 3.16 Å from the nearest metals.\(^{32}\)
Figure 2. Two views of the tetrameric aggregation of 1 (a) showing weak intermolecular contacts between Bi and O2''' and (b) the non-planar nature of the ring. Symmetry operations: ' y, 1-x, -z; " 1-x, 1-y, z; /// 1-y, x, 1-z.

The composition of 1 in solution has been probed by DOSY NMR.\textsuperscript{33} For a ca. 1 M solution in d\textsubscript{8}-toluene, the estimated molecular radius extracted from the diffusion coefficient using the Stokes-Einstein equation is 6.5 Å, which is broadly consistent with a monomeric unit taken from the structure of the tetramer (Bi-outer hydrogens ca 6.5 Å), though this is probably an overestimate of the size of a more spherical tris-chelated monomer; for example, the radius of tris-(1-methoxy-2-methyl-2-propanolato-O,O')bismuth(III) is in the range 4.4 – 5.1 Å.\textsuperscript{34} Furthermore, the accuracy of radii derived from such DOSY measurements is open to question.\textsuperscript{35} However, both the \textsuperscript{1}H and \textsuperscript{13}C NMR spectra only show one environment for the i-Pr groups at this concentration, which is also consistent with a tris-chelated monomer, though a more complex, but fluxional entity would also show this behavior. For comparison, a completely saturated solution shows very broad \textsuperscript{1}H, \textsuperscript{13}C NMR signals which may be indicative of some association of monomers. Analysis of the DOSY data for this solution is compromised by these broad signals and the tendency for the sample to start crystallizing from solution. The extrapolated molecular radius from the solution at 353 K (to minimize crystallization) is ca. 10 Å, though this assumes the
viscosity of the solution is the same as pure d$_8$-toluene which may not be true given the high
color concentration of solute. However, the collective data suggest that at high concentrations any equilibrium
between a monomer and the tetramer seen in the solid state is moving towards the latter. It should be
noted that the AACVD experiments were carried out on ca. 0.5 M solutions, and thus the "precursor
species" is almost certainly a monomeric unit.

The structure of 2 comprises a Bi$_8$O$_6$ core supported by twelve carbamate ligands (Figure 3). The
structure is complex, and comprises four distinct bismuth environments, five bonding modes for the
carbamate ligands and two types of oxo-bridges. Each of Bi(1), Bi(2) and Bi(4) is bonded to six oxygen
atoms in a distorted coordination sphere, with space evident which is presumably occupied by a lone
electron pair; though each metal also has an additional long Bi-O bond [Bi(1)-O(3): 3.058(4); Bi(2)-O(9')
2.951(4), Bi(4)-O(8) 2.798(4) Å]. Bi(3) has five short and one long Bi-O bond [Bi(3)-O(8') 2.813(4) Å] again in a distorted coordination sphere with space occupied by a lone electron pair. Bi(1) is bonded to
one chelating carbamate, one $\mu_2$-bridging carbamate, one $\mu_3$-bridging carbamate, one $\mu_4$-bridging
carbamate and two oxo-ligands, while Bi(2) is similarly ligated but with the chelating carbamate replaced
by a second $\mu_3$-bridging ligand. Bi(3) is surrounded by four bridging carbamates ($\mu_2$, two $\mu_3$, $\mu_4$) and two
oxo-ligands, while Bi(4), at the heart of the cluster, is bonded to three carbamates (two $\mu_3$, $\mu_4$) and four
lone oxygen atoms.
Figure 3. The asymmetric unit of 2 showing the labelling scheme used; thermal ellipsoids are at the 40% probability level. Selected metrical data: Bi(1)-O(1) 2.724(4), Bi(1)-O(2) 2.194(4), Bi(1)-O(3) 3.058(4), Bi(1)-O(5) 2.703(4), Bi(1)-O(12) 2.320(4), Bi(1)-O(13) 2.251(4), Bi(1)-O(15) 2.126(4), Bi(2)-O(3) 2.504(4), Bi(2)-O(4) 2.362(4), Bi(2)-O(6') 2.520(4), Bi(2)-O(7) 2.327(4), Bi(2)-O(9') 2.951(4), Bi(2)-O(13) 2.107(4), Bi(2)-O(14') 2.488(4), Bi(3)-O(5) 2.456(4), Bi(3)-O(8') 2.613(4), Bi(3)-O(10) 2.234(4), Bi(3)-O(11) 2.424(4), Bi(3)-O(14) 2.246(4), Bi(3)-O(15) 2.133(4), Bi(4)-O(3) 2.504(4), Bi(4)-O(4) 2.362(4), Bi(4)-O(5) 2.245(4), Bi(4)-O(6) 2.520(4), Bi(4)-O(7) 2.327(4), Bi(4)-O(8) 2.951(4), Bi(4)-O(9) 2.126(4), Bi(4)-O(10) 2.894(4), Bi(4)-O(11) 2.327(4), Bi(4)-O(12) 2.504(4), Bi(4)-O(13) 2.107(4), Bi(4)-O(14) 2.246(4), Bi(4)-O(14') 2.488(4), Bi(4)-O(15) 2.289(4) Å. Symmetry operation: 1-x, 1-y, -z.

The carbamate ligands divide between those which are purely chelating [e.g. κ²-O(1)/O(2)], of which there are two after symmetry considerations, those which bridge two metal centres [μ₂-O(11)/O(12), two in total], four which bridge three bismuths [μ₃-O(7)/O(8) and O(9)/O(10)], two which bridge between four metal centres [μ₄-O(5)/O(6) and its symmetry-related partner] and two which both chelate and bridge [μ₂, κ²-O(3)/O(4)]; the oxo-ligands bridge metals in either a μ₃ [O(13,15)] or μ₄-manner [O(14)].

The overall geometry is too irregular to make anything other than general comments about the bond lengths. Thus, the Bi-O bonds to the μ₂-briding carbamates [2.242(4), 2.320(4) Å] are generally shorter than those involving either the μ₄-carbamate ligands [2.456(4) – 2.703(4) Å], though the bonds involving the μ₃-ligands are highly asymmetric [2.234(4), 2.327(4), 2.687(4) - 2.951(4) Å]. Similarly, Bi-O(μ₃) tend to be shorter [2.107(4) – 2.289(4) Å] than those involving the μ₄-O [2.168(4) – 2.488(4) Å], though the situation is less clearcut around Bi(4). The κ²-ligand chelates very asymmetrically [2.149(4), 2.724(4) Å], a situation which becomes more symmetrical in the μ₂, κ²-ligand [2.362(4), 2.504(4) Å] when a long bridging interaction is added [3.058(4) Å].

Only two other examples of Bi₈-oxo clusters are cited in a recent review, namely Bi₈(O)₄(OC₆F₅)₁₆ and Bi₈(O)₄(μ-Bucalix[8]aren), both of which show lower levels of hydrolysis than 2; more recently, the structure of Bi₄(OH)₄(2,6-pdc)₄(H₂O)₂·H₂O has been reported (2,6-pdc = 2,6 pyridine dicarboxylate), which
contains a linear [Bi₆(2,6-pdc)₆]^{8+} unit in which each metal is bridged by a (2,6-pdc)^{2-} ligand. Small Bi-O clusters have been rationalized in terms of the building blocks A – C (Scheme 1), which in turn are generated from mononuclear μ₃-OBi₃ and μ₄-OBi₄ entities; the aqueous chemistry of Bi salts is dominated by the octahedron of metals in A ([Bi₆O₈]^{2+}, a motif common to hydroxyl and alkoxy derivatives), and clusters with Bi₃, Bi₆ and Bi₉ are thus relatively common. The structure of Bi₆(O)₄(OC₆F₅)₁₆ is derived from A by the addition of two, exo-octahedral bismuth atoms, converting two μ₃-OBi₃ units into μ₄-OBi₄. Bi₆(O)₄(p-Bu-calix[8]aren) is built from two B sub-units (a common feature of many observed structures) rotated 90° to each other. In contrast, the overall shape 2 can be described as derived by the loss of one metal from A to generate the square-based pyramid of metals in C ([Bi₅O₈] ), two of which, inverted with respect to each other, fuse sharing a common edge (Fig. 4).

Figure 4. The Bi₆O₆ core of 2. Symmetry operation: 1-x, 1-y, -z.

In this respect, and in terms of formula, 2 is unique among the limited examples of other Bi₆ oxo-clusters as the schematic of the core (D) highlights. This motif can, however, be discerned within [Bi₆(O)₆(OR)₆]^{5+} and the heterometallic cluster Bi₁₆Na₃(O)₁₈(OSiMe₃)₁₂.
Bismuth oxide is a remarkable material, occurring in five polymorphic forms ($\alpha$, $\beta$, $\gamma$, $\delta$ and $\omega$) of which the $\alpha$- and $\delta$-forms are considered stable while the others are metastable.\textsuperscript{41, 42} Each modification has its own properties, for example the bandgap for $\text{Bi}_2\text{O}_3$ ranges from 2.0 eV (amorphous) to 2.85 eV ($\alpha$), while $\text{BiO}$ has a bandgap of 3.31 eV;\textsuperscript{41} other authors report band gaps of 2.84 – 2.90 ($\alpha$), 2.55 – 2.75 ($\beta$), 2.68 – 2.80 ($\gamma$) and 2.93 – 3.10 ($\delta$)\textsuperscript{43} though a wider spread of values than this can be found.\textsuperscript{44}

The TGA of 1 and 2 is shown in Figure 5. For 1, the residual mass at 300 °C (32.2%) is consistent with $\text{Bi}_2\text{O}_3$ formation (theoretical residual mass 34.4%), indeed the consistency is negatively compromised slightly by a small amount of residual solvent loss (ca. 2%) at the outset of the pyrolysis. Similarly, data
for 2 show initial loss of lattice THF (theoretical loss for 6 THF per Bi₈ cluster 11.0%, observed 7.4% at 150 °C), the discrepancy probably arising from some loss of lattice THF on drying the material after synthesis; the %weight change between 150 – 400 °C (47.7%) is consistent with the transformation Bi₈(O)₂⁴(O₂CNPr')₁₂ → 4Bi₂O₃ (theoretical % loss 46.7%). Films of bismuth oxide have been deposited using 1 as precursor, by aerosol-assisted chemical vapour deposition (AACVD) onto glass substrates at temperatures between 300 and 450 °C (R1 – R4) and the outcomes analysed by PXRD (Figure 6), AFM (Figure 7) and SEM (Figure 8). At 300 °C over a 10 mins deposition time (R1), a hard, light brown/yellow, transparent film was produced which was strongly adhered to the glass substrate; PXRD can be indexed to the cubic δ-modification of Bi₂O₃ (Figure 6a). The film is smooth and featureless making it hard to image, but can be clearly seen in the SEM (edge view) of the film grown at the same temperature over a longer period (Figure 8a; see below) and is ca. 300 nm in thickness. This is in marked contrast to the elaborate hierarchical structures obtained by base hydrolysis of Bi(NO₃)₃ / NH₄VO₃ mixtures.⁴⁵ AFM analysis of this growing film shows that, after 5 mins the film comprises particles of dimension ca. 20 nm (Figure 7a,b), which become less well-defined after 10 mins growth time (Figure 7c,d); the estimated roughness of the films is ca. 6 nm. A similar morphology has been observed for β-Bi₂O₃ grown by dip coating a solution of Bi(NO₃)₃ / 2-methoxyethanol and the organic template (CH₂CH₂)₀.₆₇(CH₂CHCH₃)₀.₃₃]₈⁹(OCH₂CH₂)₇₉OH and calcined at 400 °C.⁴⁶
Figure 6. PXRD plots of the films grown from 1; bottom upwards (a) deposition at 300 °C for 10 mins (R1), (b) deposition at 300 °C for 40 mins (R2), (c) deposition at 375 °C for 40 mins (R3) and (d) deposition at 450 °C for 40 mins (R4). In (a), indexing is to cubic \( \delta \)-Bi\(_2\)O\(_3\) (PDF 77-2008), (b-d) indexed to tetragonal Bi\(_2\)O\(_3\) (PDF 78-1793), with • attributed to Bi\(_2\)O\(_{2.73}\) (PDF 76-2477) and the residue of \( \delta \)-Bi\(_2\)O\(_3\) visible but unlabelled in (b).
Figure 7. AFM analysis of the film grown from 1 at 300 °C after (a,b) 5 mins and (c,d) 10 mins deposition time. In each case the images cover a 2 x 2 µm region of the film.
When the run time is extended to 40 mins (R2), the film has a more powdery, bright yellow appearance and is poorly adhered to the glass. The PXRD is dominated by reflections which can be indexed to tetragonal $\beta$-Bi$_2$O$_3$ with some preferential orientation in the (220) direction, this latter reflection appearing significantly more intense than that of (201), the dominant line in the random pattern; the underlying $\delta$-Bi$_2$O$_3$ is still visible in the PXRD pattern, along with traces of sub-stoichiometric Bi$_{2.73}$ (Figure 6b). SEM of this film (Figure 8a,b) show both the hard underlying $\delta$-Bi$_2$O$_3$ (ca. 300 nm thick) and the growth of a more needle-like material above it (ca. 1 $\mu$m in height). It would seem that at 300 °C the formation of $\delta$-Bi$_2$O$_3$ provides a template on which $\beta$-Bi$_2$O$_3$ grows. At 375 °C (R3) and 450 °C (R4), only $\beta$-Bi$_2$O$_3$ is visible in the PXRD (save for traces of Bi$_{2.73}$), with an increasing degree of preferred (201) orientation as the temperature is raised (Figures 6c, d). The base film of $\delta$-Bi$_2$O$_3$ is still discernible in the image of the film grown at 450 °C (though it is now in such a relatively small amount as to not register in the PXRD of Figure 6d), which is now dominated by $\beta$-Bi$_2$O$_3$ fibres growing to ca. 5 $\mu$m in height (Figure 8c,d). Similar $\beta$-Bi$_2$O$_3$ nanowires have been deposited on aluminium at 300 °C by O$_2$ oxidation of bismuth.
powder heated to 800 °C over an 8 h period under an \( \text{N}_2 \) flow; however, under the same conditions at a substrate temperature of 500 °C the \( \alpha \)-modification is formed.\textsuperscript{47}

The most stable modifications of Bi\(_2\)O\(_3\) are monoclinic \( \alpha \) (up to 729 °C) and cubic \( \delta \) (stable up to 824 °C), with metastable \( \beta \)- and \( \gamma \)-forms appearing on cooling at \( T \approx 600 – 650 \) °C.\textsuperscript{48} However, CVD produces all four modifications across a range of temperatures, in which the modification adopted seems to depend on the precursor rather than temperature control (Table 2). Deposition using 1 affords the \( \delta \)-modification, an excellent oxide ion conductor and the phase with the highest conductivity,\textsuperscript{49} at the lowest temperature yet reported, with no evidence for the formation of either the \( \alpha \)- or \( \gamma \)-modifications. The \( \beta \)-modification, which is dominant at both higher temperatures and at lower temperatures over an extended run time, also has good oxide ion conductivity, surpassing that of yttria-stabilised zirconia (YST). The formation of small amounts of sub-stoichiometric Bi\(_2\)O\(_{2.73}\) is, perhaps, not surprising given 1 is acting as a true SSP.
Table 2. Bi$_2$O$_3$ phases and deposition temperatures for CVD-grown bismuth oxide$^a$

| Temperature | $\text{Bi}_3 / \text{O}_2$ | $\text{BiPh}_3 / \text{O}_2$ | $\text{BiMe}_3 / \text{O}_2$ | $\text{Bi(thd)}_3 / \text{O}_2$ | $\text{Bi(OCMe}_2\text{Et})_3$ | $\text{Bi(OBu}_3$ | 1 (this work)
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<td>200</td>
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<td></td>
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<td></td>
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<tr>
<td>250</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>420, 425</td>
<td>$\alpha + \beta^{22, e}$</td>
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<td></td>
<td></td>
<td></td>
<td>$\beta^{28}$</td>
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<td>$\alpha, \beta, \gamma^{28, e}$</td>
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<tr>
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<td>$\text{Bi}<em>2\text{O}</em>{2.33}^{12}$</td>
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<td></td>
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<td>700</td>
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<td>800</td>
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$^a$Deposition or annealing temperature depending on when the sample was analysed by PXRD. $^b$ALD. $^c$time dependent. $^d$traces $\text{Bi}_2\text{O}_{2.73}$ are also seen. $^e$product depends on gas flow rate, co-reactant $\text{H}_2\text{O}$. $^f\text{o,p-(CH}_3\text{C}_6\text{H}_4}_3\text{Bi}$ deposit $\beta$ modification at 450 °C. $^{23}$
The photocatalytic activity of bismuth oxide is well documented, with \( \alpha \), 47, 50-52 \( \beta \), 46, 47, 52-55 and \( \delta \)-polymorphs 45 being active, though the \( \beta \)-modification is considered the most active. In this work, single-phase \( \delta \)-\( \text{Bi}_2\text{O}_3 \) has been assessed by the degradation of methylene blue dye; a parallel experiment under similar conditions was carried out using a commercially marketed sample of \( \text{TiO}_2 \) on glass (NSG / Pilkington Active\textsuperscript{TM}) for comparison (Figure 9).

Figure 9. Photodegradation of only methylene blue dye (•), methylene blue dye using (♦) \( \text{TiO}_2 \) (NSG / Pilkington Activ\textsuperscript{TM}), (■) \( \delta \)-\( \text{Bi}_2\text{O}_3 \) thin film and (▲) \( \delta \)-\( \text{Bi}_2\text{O}_3 \) thin film overcoated with \( \beta \)-\( \text{Bi}_2\text{O}_3 \) nanowires, all under a 200 W HMI HR lamp; C = concentration, C(0) = concentration at time 0 sec.

The 300 nm thin film of \( \delta \)-\( \text{Bi}_2\text{O}_3 \) deposited from 1 over a 10 min period at 300 °C (R1, above) shows a very similar level of photocatalytic activity to commercial \( \text{TiO}_2 \)-coated glass, while, in contrast, that of the film deposited over a 40 min period at 450 °C – \( \beta \)-\( \text{Bi}_2\text{O}_3 \) nanowires grown over the same \( \delta \)-\( \text{Bi}_2\text{O}_3 \) base (R4, above; Figure 8c,d) – were less active. It was noted that (i) despite their visual fragility the majority of nanowires appear to remain adhered to the underlying \( \delta \)-\( \text{Bi}_2\text{O}_3 \)
film during the photodegradation experiment, but (ii) the wettability of the nanowires was significantly less than that of the δ-Bi$_2$O$_3$ film, as reflected in contact angles of 73° and 137° for the δ- and β-Bi$_2$O$_3$ films, respectively (Figure 10). Thus it seems likely that the lower photoactivity of the β-Bi$_2$O$_3$ nanowires seems to be related to the poor interface between the catalyst and the aqueous solution in this system, which in turn can be attributed to the morphology of the as-deposited material.

![Contact angles of a water droplet on (a) δ-Bi$_2$O$_3$ (b) β-Bi$_2$O$_3$.](image)

**Figure 10.** Contact angles of a water droplet on (a) δ-Bi$_2$O$_3$ (b) β-Bi$_2$O$_3$.

**Conclusions**

The bismuth carbamate Bi(O$_2$CNPr$_2$)$_3$ (1) has proved a versatile precursor for the deposition of differing modifications of Bi$_2$O$_3$ films on glass, depending on the duration and temperature of the deposition process, providing a degree of control between δ- and β-Bi$_2$O$_3$. The δ-Bi$_2$O$_3$ films show good catalytic activity (comparable to commercial TiO$_2$ NSG / Pilkington Activ™), and better than that of the deposited β-Bi$_2$O$_3$ nanowires, which have a much higher water droplet contact angle. Controlled exposure of 1 to atmospheric moisture yields the novel octa-bismuth cluster Bi$_8$(O)$_6$(O$_2$CNPr$_2$)$_{12}$ (2).

**Acknowledgements**

We thank Dr John Lowe (University of Bath) for help with the DOSY experiments and Dr Andrew Kingsley (SAFC HiTech) for recording the TGA of 1.
Supporting Information

Crystallographic data for the structural analysis (in CIF format) have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 940280, 940281 for 1, 2, respectively.

Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

References


43. E. Li, C. Lang, Z. Qiang, L. Wenhua and Y. Shuangfeng, Prog. in Chem., 2010, 22, 2282.


δ- and β-Bi₂O₃ thin films can be deposited by AACVD from a Bi(O₂CNPr²)₃ precursor, with temperature and temporal control over the deposition process. Thin δ-Bi₂O₃ films show good catalytic activity towards the photodegradation of methylene blue, while β-Bi₂O₃ nanowires are less active due to an increased hydrophobicity. Controlled hydrolysis of Bi(O₂CNPr²)₃ affords the novel oxo-cluster Bi₈(O)₆[(O₂CNPr²)₁₂].