

# The quest for mixed-metal oxide precursors based on bismuth: synthesis and molecular structure of $\text{BiTi}_2(\mu_3\text{-O})(\mu\text{-OPr}^i)_4(\text{OPr}^i)_5$ and $[\text{Bi}_2(\mu\text{-OPr}^i)_2(\text{OPr}^i)_2(\text{acac})_2]_\infty$ (acac = acetylacetonate) †

Stéphane Parola,<sup>a</sup> Renée Papiernik,<sup>a</sup> Liliane G. Hubert-Pfalzgraf,<sup>\*a</sup> Susan Jagner<sup>\*,b</sup> and Mikael Håkansson<sup>b</sup>

<sup>a</sup> Laboratoire de Chimie Moléculaire, Université de Nice-Sophia-Antipolis, 06108 – Nice, France

<sup>b</sup> Department of Inorganic Chemistry, Chalmers University of Technology, S-41296 Gothenburg, Sweden

Various routes to mixed-metal Bi–Ti species were investigated. Various heterometallic alkoxides could be isolated by using hydrolysis reactions. The mixed-metal alkoxide  $\text{BiTi}_2(\mu_3\text{-O})(\mu\text{-OPr}^i)_4(\text{OPr}^i)_5$  was obtained by reaction between titanium isopropoxide and a bismuth oxoisopropoxide formed *in situ* by controlled microhydrolysis and subsequent alcoholysis of  $\text{Bi}(\text{O}i\text{Pr})_3$ . It was characterised by X-ray crystallography, <sup>1</sup>H NMR and Fourier-transform IR spectroscopy. The structure is based on an isosceles triangular framework with a central triply bridging oxo ligand. Bismuth is four-co-ordinate with a stereochemically active lone pair. The titanium atoms are six-co-ordinate with a severely distorted octahedral environment. Synthesis and characterisation of the bismuth–titanium ethoxides  $\text{BiTi}_2\text{O}(\text{OEt})_9$  and  $\text{Bi}_4\text{Ti}_3\text{O}_4(\text{OEt})_{16}$  were achieved, as well as their evaluation as oxide precursors. The latter leads, after complete hydrolysis and thermal treatment at 450 °C, to the pure crystalline  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  perovskite phase. The synthesis and structural characterisation of  $[\text{Bi}_2(\mu\text{-OPr}^i)_2(\text{OPr}^i)_2(\eta^2\text{-acac})_2]_\infty$  (acac = acetylacetonate) are also reported. The basic structural unit is a dimer in which the five-co-ordinated metals are linked by dissymmetrical Bi–OR bridges. Each β-diketonate is chelating one metal. Chains of dimers run along the *c* axis *via* terminal semibridging isopropoxide ligands, ensuring six-co-ordination for the bismuth atoms.

An increasing number of advanced oxide materials based on bismuth appear to display attractive properties. The ferroelectrics such as  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  and  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  illustrate these features.<sup>1</sup> However, chemical routes to such materials remain scarce, probably as a result of the non-commercial availability of bismuth alkoxides. Bismuth acetate or nitrate are thus the most commonly used sources of bismuth oxide for access to bismuth materials by solution routes. Mixed-metal alkoxides based on bismuth are rare although such species could act as ‘single-source’ precursors.<sup>2</sup> They are restricted to the alkali-metal species  $\text{Na}_4\text{Bi}_2\text{O}(\text{O}i\text{Pr})_8$ ,  $\text{KBi}(\text{O}i\text{Pr})_4$ ,<sup>3</sup>  $\text{NaBi}_3\text{O}(\text{OC}_6\text{F}_5)_8(\text{thf})$  (thf = tetrahydrofuran),  $\text{Na}_2\text{Bi}_4\text{O}_2(\text{OC}_6\text{F}_5)_{10}$  and  $\text{NaBi}_4\text{O}_2(\text{OC}_6\text{F}_5)_9(\text{thf})_2$ ,<sup>4,5</sup> and one transition-metal species  $[\text{Cl}_3\text{BiOV}(\text{OC}_2\text{H}_4\text{OMe})_3]_2$ .<sup>6</sup> Only the latter implies metals related to materials.

We now report the synthesis and structural characterisation of the first bismuth–titanium heterometallic species,  $\text{BiTi}_2(\mu_3\text{-O})(\mu\text{-OPr}^i)_4(\text{OPr}^i)_5$ , which was previously mentioned by us in a preceding<sup>7</sup> and of  $[\text{Bi}_2(\mu\text{-OPr}^i)_2(\text{OPr}^i)_2(\eta^2\text{-acac})_2]_\infty$  (acac = acetylacetonate). Evaluation of the behaviour of Bi–Ti ethoxides in hydrolytic polycondensation reactions was achieved.

## Results and Discussion

### Synthesis

The mixing of homometallic alkoxides has traditionally been considered as the simplest route to the formation of mixed-metal species and thus to achievement of homogeneity at a molecular level.<sup>2,8</sup> Another usual route to mixed-metal species is the metathesis reaction between metal halides and alkali-metal alkoxides. However the reactions between  $\text{NaTi}(\text{OPr}^i)_5$  and  $\text{BiX}_3$  (X = Cl or Br) in tetrahydrofuran, toluene or in the parent

alcohol, at room temperature, proceed by transmetallation giving  $\text{Ti}(\text{OPr}^i)_4$  and insoluble  $\text{Bi}(\text{OPr}^i)_3$  (evidence by Fourier-transform IR and <sup>1</sup>H NMR spectroscopy). Lewis acid–base reactions are considered to occur easily even for polymeric metal alkoxides.<sup>2</sup> Bismuth alkoxides,  $\text{Bi}(\text{OR})_3$  (R = Et or Pr<sup>i</sup>), however remain insoluble in toluene in the presence of  $\text{Ti}(\text{OR})_4$ ; similar observations were made for  $\text{Bi}(\text{OPr}^i)_3$  in the presence of other transition-metal alkoxides such as  $\text{Nb}(\text{OPr}^i)_5$  and  $\text{VO}(\text{OPr}^i)_3$ . Addition of the parent alcohol allowed partial dissolution of bismuth isopropoxide, but no mixed-metal species are formed as shown by Fourier-transform IR and <sup>1</sup>H NMR spectroscopy. Attempts to induce a reaction by heating led to the partial decomposition of the bismuth alkoxide, especially for the isopropoxide, with formation of metal particles. Dissolution of bismuth alkoxides can also be induced by trace amounts of water. Reactive bismuth species were obtained by controlled microhydrolysis {hydrolysis ratio = 0.2–0.7,  $h = [\text{H}_2\text{O}]/[\text{Bi}(\text{OR})_3]$ } of  $\text{Bi}(\text{O}i\text{Pr})_3$  in toluene and subsequent alcoholysis. Thus the bismuth oxoisopropoxide species **1**, derived from microhydrolysis of  $\text{Bi}(\text{O}i\text{Pr})_3$  ( $h = 0.2$ ) and reaction with Pr<sup>i</sup>OH, reacts with  $\text{Ti}(\text{OPr}^i)_4$  in toluene at room temperature. A new species  $\text{BiTi}_2(\mu_3\text{-O})(\mu\text{-OPr}^i)_4(\text{OPr}^i)_5$  **2**, containing bismuth and titanium, was isolated by addition of Pr<sup>i</sup>OH (≈30% yield). The Fourier-transform IR spectra show differences between  $\text{Bi}(\text{OPr}^i)_3$ , **1** and **2** in the region attributed to M–OR vibrations. The spectrum of  $\text{Bi}(\text{OPr}^i)_3$  shows five strong absorption bands at 565, 540, 450, 434 and 410 cm<sup>−1</sup> while that of **1** shows only one strong and broad band around 400 cm<sup>−1</sup>. Compound **2** displays many bands related to Bi–OR and Ti–OR vibrations between 586 and 405 cm<sup>−1</sup>. Bismuth–titanium ethoxides were prepared in the same way as for **2** with hydrolysis ratios varying from 0.2 to 0.7, but species of different stoichiometries were isolated. Indeed while only one species,  $\text{BiTi}_2\text{O}(\text{OPr}^i)_9$ , could be isolated with isopropoxides, the reactions with ethoxides afforded  $\text{BiTi}_2\text{O}(\text{OEt})_9$ , **3** and  $\text{Bi}_4\text{Ti}_3\text{O}_4$ -

† Non-SI unit employed: Torr ≈ 133 Pa.

(OEt)<sub>16</sub>, **4** according to elemental analysis. They were separated by their difference in solubility. The formation of **4** is favored by the increase of the hydrolysis ratio. When  $0.2 < h < 0.4$ , **3** is the predominant species (43%). With  $h$  values higher than 0.4, **4** is the major product of the reaction (38%). The overall observations suggest that the formation of Bi–Ti species proceeds *via* bismuth oxoalkoxides, the latter being the true reactive species and not the initial bismuth alkoxide.<sup>8</sup> Reinvestigations of systems involving polymeric metal alkoxides, for instance based on late transition metals, have also shown the importance of water in the formation of mixed-metal species.<sup>9</sup> A few bismuth oxo-species are known, namely [Bi<sub>6</sub>O<sub>2</sub>(OC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Bi(OC<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>3</sub>L<sub>2</sub> (L = tetrahydrofuran or toluene),<sup>4</sup> [Bi<sub>6</sub>O<sub>3</sub>(OC<sub>6</sub>F<sub>5</sub>)<sub>12</sub>(thf)<sub>2</sub>],<sup>5</sup> [Bi<sub>4</sub>O<sub>2</sub>(OBu)<sub>8</sub>]<sup>10</sup> and more recently [Bi<sub>6</sub>O<sub>3</sub>(OR)<sub>12</sub>] (R = 2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).<sup>11</sup> Unfortunately no crystals suitable for X-ray diffraction could be grown for **1**.

The <sup>1</sup>H NMR spectra of compound **2** are uninformative even at low temperature (–40 °C) since the methine groups appear as an unique septuplet at δ 4.5 (in CDCl<sub>3</sub>) or as two broad multiplets (in [<sup>2</sup>H<sub>8</sub>] toluene), probably as a result of the relaxation effects of the quadrupolar metal nuclei. The spectra of **3** at –40 °C in CDCl<sub>3</sub> show three multiplets in the CH<sub>2</sub> region in an 2:6:1 integration ratio, which can be attributed to different types of ethoxide ligands. The low-temperature NMR spectra of **4** also present three multiplets in this region but with integration ratio 4:10:2.

The reactions between metal alkoxides and carboxylates or β-diketonates were investigated as another route to heterometallic species.<sup>9</sup> No mixed-metal species could be isolated by treating Bi(O<sub>2</sub>CMe)<sub>3</sub> with Ti(OR)<sub>4</sub> (R = Pr<sup>i</sup>, Et or C<sub>2</sub>H<sub>4</sub>OMe) in toluene, pyridine or alcohols (HOC<sub>2</sub>H<sub>4</sub>OMe or HOC<sub>2</sub>H<sub>4</sub>OPr<sup>i</sup>) at room temperature. Heating of the solution often led to partial decomposition of the bismuth species. The use of 2-methoxyethanol induces dissolution upon heating but no species could be crystallised.

Bismuth acetylacetonate reacts with titanium isopropoxide in toluene at room temperature. The compounds isolated by their difference in solubility correspond to homometallic species resulting from ligand-exchange reactions: Ti(OPr<sup>i</sup>)<sub>2</sub>(acac)<sub>2</sub> was formed whereas the bismuth compound corresponds to [Bi<sub>2</sub>(O-Pr<sup>i</sup>)<sub>4</sub>(acac)<sub>2</sub>]<sub>n</sub>, **5**. The IR spectrum of **5** shows absorption bands in the C–O vibration region at 1604, 1541 and 1509 cm<sup>-1</sup>. There are two additional bands in the M–OR region at 551 and 388 cm<sup>-1</sup> with respect to the spectrum of Bi(OPr<sup>i</sup>)<sub>3</sub>, while the band observed at 434 cm<sup>-1</sup> for Bi(OPr<sup>i</sup>)<sub>3</sub> is shifted to 425 cm<sup>-1</sup> for **5**. The <sup>1</sup>H NMR spectra at room temperature show one singlet at δ 5.26 which can be attributed to the CH groups of the β-diketonate, and one multiplet at δ 5.2 assigned to the methine groups of the isopropoxide ligands, with respective integration ratios of 1:2.

### Structural characterisations

X-ray diffraction studies established compound **2** to be BiTi<sub>2</sub>(μ<sub>3</sub>-O)(μ-OPr<sup>i</sup>)<sub>4</sub>(OPr<sup>i</sup>)<sub>5</sub> as shown in Fig. 1. Selected bond lengths and angles are collected in Table 1. The structure is based on an isosceles triangular framework [Bi···Ti distance of 3.23 Å average, Ti(1)···Ti(2) 2.970(4) Å] with a central triply bridging oxo ligand O(1). The sum of the angles around the oxo ligand (Σ = 301.1°) accounts for a pyramidal stereochemistry. Bismuth and titanium are connected by a single doubly bridging isopropoxide ligand while the two titanium atoms are connected by two μ-OPr<sup>i</sup> groups, thus ensuring six-co-ordination for the transition metals. Bismuth is four-co-ordinate with O–Bi–O angles ranging from 69.1(3) to 129.4(3)° and a stereochemically active lone pair. The metal–oxygen bond lengths spread over the range 1.77(1) to 2.351(9) Å, the order of variation being Ti–OR(t) < μ-Ti–OR–(Bi) < Ti–μ<sub>3</sub>-O < μ-Ti–OR–(Ti) < Bi–μ<sub>3</sub>-O ≈ Bi–OR(t) < Bi–μ-OR. The values observed are in agreement with literature data.<sup>3–6,12</sup> The environment of the titanium

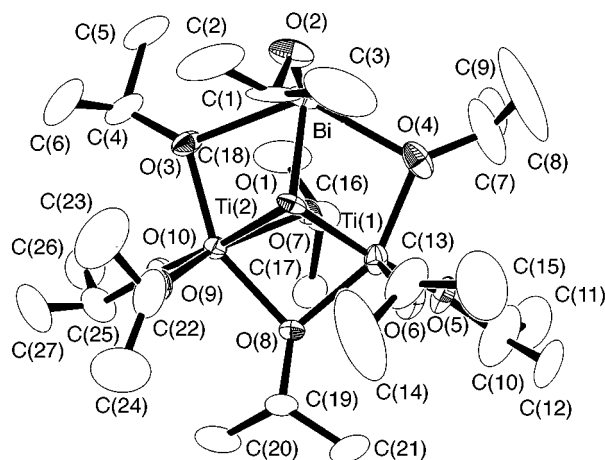


Fig. 1 Molecular structure of BiTi<sub>2</sub>(μ<sub>3</sub>-O)(μ-OPr<sup>i</sup>)<sub>4</sub>(OPr<sup>i</sup>)<sub>5</sub> showing the atom numbering scheme

Table 1 Selected bond lengths (Å) and angles (°) for BiTi<sub>2</sub>(μ<sub>3</sub>-O)(μ-OPr<sup>i</sup>)<sub>4</sub>(OPr<sup>i</sup>)<sub>5</sub>

Bi···Ti(1)	3.231(3)	Bi···Ti(2)	3.229(3)
Bi–O(1)	2.090(8)	Bi–O(2)	2.10(1)
Bi–O(3)	2.351(9)	Bi–O(4)	2.36(1)
Ti(1)···Ti(2)	2.970(4)	Ti(1)–O(1)	2.035(9)
Ti(1)–O(4)	1.98(1)	Ti(1)–O(5)	1.77(1)
Ti(1)–O(6)	1.814(9)	Ti(1)–O(7)	2.154(8)
Ti(1)–O(8)	2.035(9)	Ti(2)–O(1)	2.015(9)
Ti(2)–O(3)	1.975(9)	Ti(2)–O(7)	2.159(8)
Ti(2)–O(8)	2.060(9)	Ti(2)–O(9)	1.788(9)
Ti(2)–O(10)	1.803(9)		
O(1)–Ti(1)–O(4)	78.2(4)	O(4)–Ti(1)–O(7)	85.5(3)
O(1)–Ti(1)–O(5)	165.2(4)	O(4)–Ti(1)–O(8)	152.8(4)
O(1)–Ti(1)–O(6)	95.7(4)	O(5)–Ti(1)–O(6)	99.1(5)
O(1)–Ti(1)–O(7)	70.2(3)	O(5)–Ti(1)–O(7)	95.4(4)
O(1)–Ti(1)–O(8)	78.7(3)	O(5)–Ti(1)–O(8)	101.2(4)
O(4)–Ti(1)–O(5)	97.5(5)	O(6)–Ti(1)–O(7)	164.0(4)
O(4)–Ti(1)–O(6)	99.1(5)	O(6)–Ti(1)–O(8)	97.3(4)
O(1)–Ti(2)–O(3)	77.7(3)	O(7)–Ti(1)–O(8)	73.2(3)
O(1)–Ti(2)–O(7)	70.5(3)	O(3)–Ti(2)–O(10)	95.2(4)
O(1)–Ti(2)–O(8)	78.6(3)	O(7)–Ti(2)–O(8)	72.6(3)
O(1)–Ti(2)–O(9)	95.8(4)	O(7)–Ti(2)–O(9)	162.6(4)
O(1)–Ti(2)–O(10)	163.6(4)	O(7)–Ti(2)–O(10)	94.5(4)
O(3)–Ti(2)–O(7)	85.7(4)	O(8)–Ti(2)–O(10)	94.6(4)
O(3)–Ti(2)–O(8)	152.1(4)	O(8)–Ti(2)–O(10)	103.7(4)
O(3)–Ti(2)–O(9)	102.2(4)	O(9)–Ti(2)–O(10)	100.1(4)
O(1)–Bi–O(2)	91.3(3)	O(2)–Bi–O(3)	101.7(4)
O(1)–Bi–O(3)	68.3(3)	O(2)–Bi–O(4)	105.3(4)
O(1)–Bi–O(4)	69.1(3)	O(3)–Bi–O(4)	129.4(3)
Bi–O(1)–Ti(1)	103.1(4)	Bi–O(3)–Ti(2)	96.2(4)
Bi–O(1)–Ti(2)	103.7(4)	Bi–O(4)–Ti(1)	96.1(4)
Ti(1)–O(1)–Ti(2)	94.3(4)	Ti(1)–O(7)–Ti(2)	87.0(3)
Ti(1)–O(8)–Ti(2)	93.0(4)		

atoms is severely distorted as shown by the O–Ti–O angles ranging from 70.2(3) to 165.2(4)°. The overall structure can formally be considered as resulting from the association of the bismuth oxoalkoxide BiO(OR) with a dinuclear Ti<sub>2</sub>(OPr<sup>i</sup>)<sub>8</sub> unit or of the [Ti<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>]<sup>–</sup> and BiO<sup>+</sup> ions. The BiTi<sub>2</sub>(μ<sub>3</sub>-O)(μ-OPr<sup>i</sup>)<sub>4</sub>(OPr<sup>i</sup>)<sub>5</sub> clusters appear linked by a very weak Bi···O interaction [Bi–O(2\*) 3.10(1) Å; \* –x, –y, 2–z]. Two types of structural models are known for species displaying a MM'<sub>2</sub> stoichiometry, either an open-shell core such as MNb<sub>2</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(OPr<sup>i</sup>)<sub>10</sub> (M = Mg or Cd),<sup>13</sup> BaNb<sub>2</sub>(OPr<sup>i</sup>)<sub>12</sub>(HOPr<sup>i</sup>)<sub>2</sub>,<sup>14</sup> or Al<sub>2</sub>Hf(OPr<sup>i</sup>)<sub>10</sub>,<sup>15</sup> or a triangular core generally stabilised by two triply bridging ligands such as NaCe<sub>2</sub>(OBu)<sub>9</sub>,<sup>16</sup> YCl<sub>2</sub>[Ti<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>] and CuCl[Ti<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>].<sup>17</sup> The compound BiTi<sub>2</sub>O(OPr<sup>i</sup>)<sub>9</sub> shows a triangular framework but with only one central triply bridging oxo ligand instead of the two μ<sub>3</sub>-OR usually observed. The NMR data support the retention of the trinuclear solid-

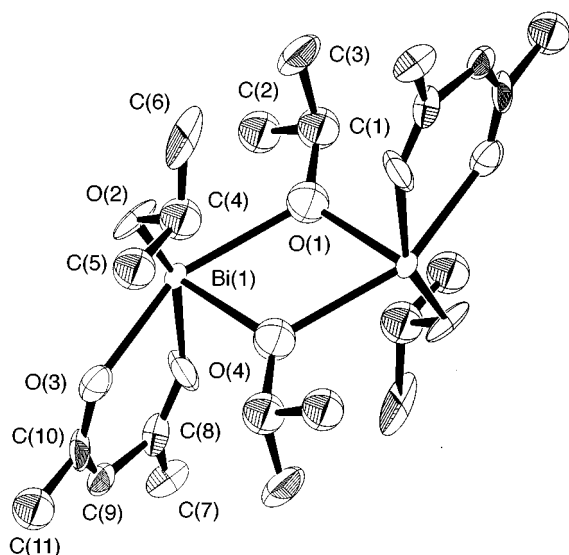


Fig. 2 Basic structural unit of  $[\text{Bi}_2(\mu\text{-OPr})_2(\text{OPr})_2(\eta^2\text{-acac})_2]_\infty$  showing the atom numbering scheme

Table 2 Selected bond lengths (Å) and angles (°) for  $\text{Bi}_2(\mu\text{-OPr})_2(\text{OPr})_2(\eta^2\text{-acac})_2$

Bi(1)–O(1*)	2.50(2)	C(1)–C(2)	1.51(5)
Bi(1)–O(1)	2.19(2)	C(1)–C(3)	1.54(6)
Bi(1)–O(2)	2.12(3)	C(4)–C(5)	1.54(5)
Bi(1)–O(3)	2.27(3)	C(4)–C(6)	1.40(6)
Bi(1)–O(4)	2.43(4)	C(7)–C(8)	1.47(6)
O(1)–C(1)	1.46(4)	C(8)–C(9)	1.50(6)
O(2)–C(4)	1.45(5)	C(9)–C(10)	1.34(6)
O(3)–C(10)	1.26(5)	C(10)–C(11)	1.55(6)
O(4)–C(8)	1.21(5)	Bi(1)⋯Bi(1')	3.95(1)
Bi(1)–Bi(1*)	3.92(1)		
O(1)–Bi(1)–O(1*)	67.0(9)	O(1)–C(1)–C(2)	107(3)
O(1)–Bi(1)–O(2)	95(1)	O(1)–C(1)–C(3)	109(4)
O(1)–Bi(1)–O(3)	153.8(8)	O(2)–C(4)–C(5)	109(3)
O(1)–Bi(1)–O(4)	103(1)	O(2)–C(4)–C(6)	106(3)
O(1*)–Bi(1)–O(2)	93(1)	O(2)–C(8)–C(7)	129(4)
O(1*)–Bi(1)–O(3)	87.0(9)	O(4)–C(8)–C(9)	119(4)
O(1*)–Bi(1)–O(4)	91(1)	O(3)–C(10)–C(9)	132(4)
O(2)–Bi(1)–O(3)	88(1)	O(3)–C(10)–C(11)	112(4)
O(2)–Bi(1)–O(4)	161(1)	O(3)–Bi(1)–O(4)	73(1)
Bi(1)–O(1)–Bi(1*)	113.0(9)	Bi(1)–O(2)–C(4)	124(2)
Bi(1)–O(1)–C(1)	123(2)	Bi(1)–O(3)–C(10)	134(3)
Bi(1*)–O(1)–C(1)	124(2)	Bi(1)–O(4)–C(8)	139(3)

Symmetry operators: \*  $-x, -y, -z$ .

state structure upon dissolution. No signals corresponding to  $\text{Bi}(\text{OPr})_3$  ( $\delta$  4.0) or to  $\text{Ti}(\text{OPr})_4$  ( $\delta$  4.2) were observed for the methine groups.

The poor quality of the crystals of compounds **3** and **4** precluded studies by single-crystal X-ray diffraction. Proton NMR data for **3** indicate three types of  $\text{CH}_2$  and thus support a framework similar to that of **2**. Four types of OR groups are expected while only three are observed (2:6:1 integration ratio). These data are consistent with fast exchange on the NMR time-scale between the two bridging Ti–OR–Ti and the four terminal Ti–OR ligands. No structural model can be given for compound **4** since no mixed-metal species having a 4:3 stoichiometry between the metals is known to the best of our knowledge. Investigations using WAXS (wide angle X-ray scattering) studies are in progress for **4**.

The compound  $[\text{Bi}_2(\text{OPr})_4(\text{acac})_2]_\infty$  **5** could also be characterised by X-ray diffraction studies. Selected bond lengths and angles are given in Table 2. The basic structural unit is a dimer (Fig. 2); the metals are linked by two bridging isopropoxide ligands forming a quite dissymmetrical bridge [Bi(1)–O(1)

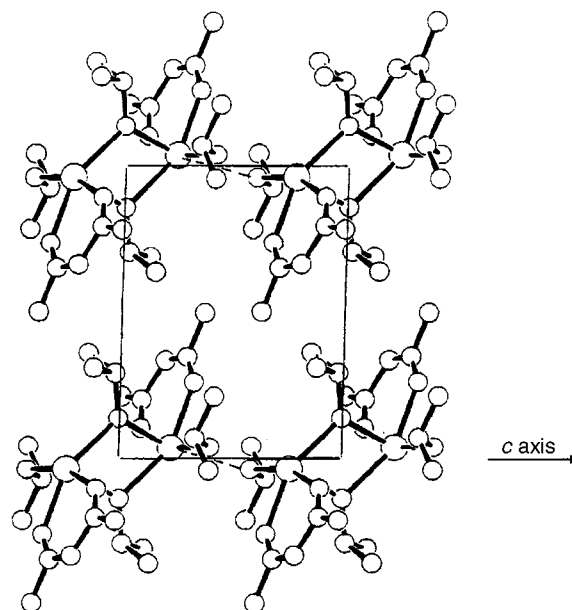


Fig. 3 Interactions between  $\text{Bi}_2(\text{OPr})_4(\text{acac})_2$  units along the  $c$  axis (dotted lines represent the intermolecular interactions) [2.69(3) Å]

2.19(2) and Bi(1)–O(1\*) 2.50(2) Å]. Each metal atom bears one  $\eta^2$ -acac ligand, one terminal and two bridging OR groups. The bismuth–oxygen distances spread over the range 2.12(3) to 2.50(2) Å following the order Bi–OR(t) < Bi– $\mu$ -O(1)R < Bi–O(acac) < Bi– $\mu$ -O(1\*)R. The bismuth atoms appear at first glance five-co-ordinate with a stereochemically active lone pair. However, examination of the intermolecular contacts show short distances of 2.69(3) Å (as compared to the sum of the van der Waals radii  $\approx$  3.47 Å) between Bi(1) and O(2) of a neighbouring dimer. The overall structure thus consists of chains of dimers (Fig. 3) developing along the  $c$  axis via terminal isopropoxide ligands which can actually be considered as semibridging ligands.<sup>18</sup> The non-bonding Bi⋯Bi distances within the dimers and along the chains are 3.92(1) and 3.95(2) Å respectively. Similar intermolecular interactions and unsymmetrical bridges were observed for  $[\text{Bi}_2(\mu\text{-OC}_2\text{H}_4\text{OMe})_4(\text{OC}_2\text{H}_4\text{OMe})_2]_\infty$ .<sup>19</sup> The formation of the chains increases the co-ordination number of bismuth which is actually six-co-ordinate and explains the lack of volatility of the bismuth acetylacetonatoisopropoxide [up to 100 °C ( $10^{-4}$  Torr), where decomposition of **5** into metallic bismuth occurred] as compared to  $[\text{Bi}(\text{OPr})_3]_m$  [ $\approx$  100 °C ( $10^{-4}$  Torr)]. Compound **5** is isostructural to  $[\text{Bi}(\text{OC}_6\text{F}_5)_3(\text{C}_6\text{H}_5\text{Me})_2]_2\cdot 2\text{C}_6\text{H}_5\text{Me}$  which was previously reported by Whitmire and co-workers.<sup>20</sup>

### Hydrolysis–polycondensation reactions

The hydrolysis–polycondensation reactions of the various Bi–Ti alkoxides were investigated. Hydrolysis of compound **2** in  $\text{Pr}'\text{OH}$  ( $h = 18$ ) gave an amorphous powder. Its thermal treatment afforded the pyrochlore  $\text{Bi}_2\text{Ti}_2\text{O}_7$  at 650 °C and  $\text{Bi}_2\text{Ti}_4\text{O}_{11}$  above 900 °C as analysed by powder X-ray diffraction. Studies on the powder resulting from the hydrolysis of the ethoxide analog  $\text{BiTi}_2\text{O}(\text{OEt})_9$  **3** gave different results. Thermal annealing of the powder resulting from the complete hydrolysis of **3** afforded  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  at 1000 °C with  $\text{Bi}_2\text{Ti}_4\text{O}_{11}$  impurities. The pure crystalline perovskite  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  was obtained at 450 °C by using **4** as the precursor. This observation confirms the 4/3 stoichiometry between the two metals in the precursor (absence of other phases, either crystalline or amorphous). The temperature of crystallisation, which is comparable to that obtained while using bismuth and titanium 2-methoxyethoxide solutions,<sup>21</sup> is quite low by comparison to the value of 700 °C reported on using a mixture of bismuth and titanium precursors, namely  $\text{Bi}(\text{O}_2\text{CMe})_3$  and  $\text{Ti}(\text{OC}_2\text{H}_4\text{OMe})_4$ ,  $\text{Bi}(\text{OEt})_3$

and  $\text{Ti}(\text{OBU}^n)_4$ , or  $\text{Bi}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Ti}(\text{OPr}^i)_4$ .<sup>22</sup> It emphasises the benefit of using single-source precursors for chemical routes to multicomponent oxides.

## Conclusion

The formation of mixed-metal alkoxides can be induced by controlled hydrolysis. This activation of metal alkoxides inert toward Lewis acid–base reactions with other metal species, namely bismuth ones here, occurs spontaneously in material science where commercial solvents, and thus containing some water, are generally used. The use of a ‘single-source’ precursor having a stoichiometry between the metals matching that of the final material allows one to reduce the temperature of crystallisation of the materials especially if the metals are already assembled by oxo ligands.

## Experimental

All reactions were conducted under an inert atmosphere using Schlenk tubes and vacuum-line techniques. Solvents were purified by standard techniques. The compound  $\text{Bi}(\text{OBU}^i)_3$  was prepared according to the literature<sup>19</sup> and  $\text{Ti}(\text{OR})_4$  ( $\text{R} = \text{Et}$  or  $\text{Pr}^i$ ) (Aldrich) were distilled before use. Infrared spectra were recorded on a Bruker IR-45S spectrometer as Nujol mulls, NMR spectra on a Bruker AC-200 spectrometer. Analyses were done at the Centre de Microanalyses du CNRS. Powder X-ray diffraction patterns were obtained on a Siemens D5000 diffractometer.

### Syntheses

**$\text{BiTi}_2\text{O}(\text{OPr}^i)_9$ , **2**.** Typically a toluene–water solution ( $2.4 \times 10^{-2}$  mol  $\text{dm}^{-3}$  water, 20  $\text{cm}^3$ ) was added at room temperature to  $\text{Bi}(\text{OBU}^i)_3$  (1.04 g, 2.43 mmol) in toluene (15  $\text{cm}^3$ ). The reaction medium was stirred for 15 h and evaporated to dryness. The resulting powder was dissolved in toluene (10  $\text{cm}^3$ ) and  $\text{Pr}^i\text{OH}$  (2  $\text{cm}^3$ ) was added; after  $\approx 30$  min the solvent was removed. The compound  $\text{Ti}(\text{OPr}^i)_4$  (0.69 g, 2.43 mmol) in toluene (10  $\text{cm}^3$ ) was added to the suspension of the bismuth derivative in toluene (10  $\text{cm}^3$ ). After 24 h, the mixture was filtered and crystallisation of **2** was obtained by adding  $\text{Pr}^i\text{OH}$  (0.5  $\text{cm}^3$ ) and cooling at  $-20^\circ\text{C}$  (0.6 g, 30%). IR ( $\text{cm}^{-1}$ ): 1324, 1163, 1131, 1005, 965, 945, 851, 827, 694, 611, 586, 554, 528, 500, 477, 429, 405 [ $\nu(\text{M}-\text{OR})$ ].  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $-40^\circ\text{C}$ ):  $\delta$  4.5 (spt, CH, 9 H,  $J = 6.1$ ) and 1.25 (d,  $\text{CH}_3$ , 54 H,  $J = 6.1$  Hz) (Found: C, 37.97; H, 7.45; Bi, 23.85; Ti, 12.71. Calc. for  $\text{C}_{27}\text{H}_{63}\text{BiO}_{10}\text{Ti}_2$ : C, 38.04; H, 7.45; Bi, 24.54; Ti, 12.71%).

**$\text{BiTi}_2\text{O}(\text{OEt})_9$ , **3**.** The same procedure was applied to  $\text{Bi}(\text{OBU}^i)_3$  (2.1 mmol), with a hydrolysis ratio  $h = 0.2$ ,  $\text{HOEt}$  and  $[\text{Ti}(\text{OEt})_4]_3$  (0.7 mmol) in toluene. The crude product was dissolved in hexane (5  $\text{cm}^3$ ). Crystallisation of compound **3** was achieved by adding ethanol (0.1  $\text{cm}^3$ ) and cooling at  $-20^\circ\text{C}$  [0.65 g, 43% based on  $\text{Bi}(\text{OR})_3$ ]. IR ( $\text{cm}^{-1}$ ): 1145, 1096, 1053, 1015, 923, 900, 883, 850, 593, 429 [ $\nu(\text{M}-\text{OR})$ ].  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $-40^\circ\text{C}$ ):  $\delta$  4.65, 4.3, 4.05 (m,  $\text{CH}_2$ , 18 H, 4:12:2), 1.2 (m,  $\text{CH}_3$ , 18 H) (Found: C, 30.03; H, 6.7; Bi, 27.79; Ti, 12.86. Calc. for  $\text{C}_{18}\text{H}_{45}\text{BiO}_{10}\text{Ti}_2$ : C, 29.8; H, 6.2; Bi, 28.79; Ti, 13.2%).

**$\text{Bi}_4\text{Ti}_3\text{O}_4(\text{OEt})_{16}$ , **4**.** The same procedure was applied to  $\text{Bi}(\text{OBU}^i)_3$  (4.8 mmol) with a hydrolysis ratio  $h = 0.7$ ,  $\text{HOEt}$  and  $[\text{Ti}(\text{OEt})_4]_3$  (1.59 mmol) in toluene. The powder was dissolved in hexane (5  $\text{cm}^3$ ) and ethanol (0.5  $\text{cm}^3$ ). Compound **3** crystallised first at  $-20^\circ\text{C}$  [0.19 g, 5.42% based on  $\text{Bi}(\text{OR})_3$ ], then crystals of **4** were obtained at  $-20^\circ\text{C}$  [0.8 g, 38% based on  $\text{Bi}(\text{OR})_3$ ]. IR ( $\text{cm}^{-1}$ ): 1145, 1036, 1053, 1015, 968, 924, 895, 801, 648, 574, 364 [ $\nu(\text{M}-\text{OR})$ ].  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $-40^\circ\text{C}$ ):  $\delta$  4.40, 4.20, 3.80 (m,  $\text{CH}_2$ , 32 H, 8:20:4), 1.3–1.1 (overlapping triplets,  $\text{CH}_3$ , 48 H) (Found: C, 17.69; H, 3.70; Bi, 47.74; Ti, 8.13. Calc. for  $\text{C}_{32}\text{H}_{80}\text{Bi}_4\text{O}_{20}\text{Ti}_3$ : C, 21.77; H, 4.53; Bi, 47.4; Ti, 8.15%). Com-

**Table 3** Crystallographic data for  $\text{BiTi}_2(\mu_3\text{-O})(\mu\text{-OPr}^i)_4(\text{OPr}^i)_5$  and  $\text{Bi}_2(\mu\text{-OPr}^i)_2(\text{OPr}^i)_2(\eta^2\text{-acac})_2$

Chemical formula	$\text{C}_{27}\text{H}_{63}\text{O}_{10}\text{BiTi}_2$	$\text{C}_{22}\text{H}_{40}\text{O}_8\text{Bi}_2$
<i>M</i>	852.57	425.26
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
<i>Z</i>	4	2
<i>a</i> /Å	10.291(3)	9.89(5)
<i>b</i> /Å	20.768(2)	10.49(5)
<i>c</i> /Å	17.759(4)	7.12(2)
$\alpha$ /°		97.2(3)
$\beta$ /°	90.76(2)	90.9(3)
$\gamma$ /°		71.0(4)
<i>U</i> /Å <sup>3</sup>	3795(1)	693(5)
<i>F</i> (000)	1728	402
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.492	2.039
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	50.61	126.85
Temperature/°C	-110	-100
<i>R</i> <sup>a</sup>	0.048	0.087
<i>R</i> ' <sup>b</sup>	0.051	0.115

$$^a \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad ^b [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}.$$

pounds **2–4** are soluble in common organic solvents and alcohols.

**$[\text{Bi}_2(\mu\text{-OPr}^i)_2(\text{OPr}^i)_2(\eta^2\text{-acac})_2]_\infty$ , **5**.** Bismuth acetylacetonate [prepared by treating acetylacetonone (2.38 mmol) with  $\text{Bi}(\text{OBU}^i)_3$  (0.8 mmol) in toluene (5  $\text{cm}^3$ )] was dissolved in toluene (15  $\text{cm}^3$ ) and  $\text{Ti}(\text{OPr}^i)_4$  (0.23 g, 0.8 mmol) in toluene (5  $\text{cm}^3$ ) was added. After concentration, colourless cubes poorly soluble in toluene and ether, but soluble in thf, were obtained at  $5^\circ\text{C}$  (0.25 g, 73.5%). The same product was prepared by treating Hacac with  $\text{Bi}(\text{OPr}^i)_3$  (1:1 stoichiometry) in toluene. IR ( $\text{cm}^{-1}$ ): 1604, 1541, 1509 [ $\nu(\text{C}=\text{O})$ ]; 1356, 1338, 1239, 1196, 1164, 1115, 1015, 945, 923, 827, 767, 726, 649, 577, 551, 536, 447, 425, 410, 388 [ $\nu(\text{M}-\text{OR})$ ].  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.26 (s, 1 H, CH), 5.2 (m, CH,  $\text{Pr}^i$ , 2 H), 1.98 (s,  $\text{CH}_3$ , acac, 6 H) and 1.23 (d,  $\text{CH}_3$ ,  $\text{Pr}^i$ , 12 H,  $J = 6$  Hz).

### Crystallography

Crystals were mounted using low-temperature methodology.<sup>23</sup> Measurements were made at 163 K on a Rigaku AFC6R diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and the  $\omega$ - $2\theta$  scan mode with an  $\omega$ -scan rate of  $32^\circ \text{min}^{-1}$  for compound **2** and of  $8^\circ \text{min}^{-1}$  for **5** and a scan width of  $(1.31 + 0.30 \tan \theta)^\circ$ . Unit-cell dimensions were determined from the setting angles of 25 reflections in the range  $25.7 < 2\theta < 30.48^\circ$  for **2** and 5 reflections in the range  $11.0 < 2\theta < 14.7^\circ$  for **5**. The structures were solved by direct methods (MITHRIL)<sup>24</sup> and full-matrix least-squares refinement of positional and anisotropic thermal parameters. All calculations were carried out with the TEXSAN crystallographic software package.<sup>25</sup> It was not possible to correct the data for the effects of absorption.

CCDC reference number 186/734.

### Acknowledgements

This work was supported by the Swedish Institute and Chalmers University of Technology.

### References

- S. L. Swartz and V. E. Wood, *Condensed Matter News*, 1992, **1**, 4; F. M. Ross, K. M. Krishnan, N. Thangaraj, R. F. C. Farrow, R. F. Marks, A. Cebollada, S. S. P. Parkin, M. F. Toney, M. Huffman, C. A. Paz De Araujo, L. D. Mc Millan, J. Cuchiaro, M. C. Scott, C. Echer, F. Ponce, M. A. O'Keefe and F. C. Nelson, *Mater. Res. Soc. Bull.*, 1996, **21**, 17.
- K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969.

- 3 M. Veith, E. C. Yu and V. Huch, *Chem. Eur. J.*, 1995, **1**, 27.
- 4 C. M. Jones, M. D. Burkart and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1992, 1638.
- 5 K. H. Whitmire, C. M. Jones, M. D. Burkart, J. C. Hutchinson and A. L. McKnight, *Mater. Res. Soc. Proc.*, 1992, **271**, 149.
- 6 J. W. Pell, W. C. Davis and H. C. zur Loye, *Inorg. Chem.*, 1996, **35**, 5734.
- 7 R. Papiernik, L. G. Hubert-Pfalzgraf, S. Parola, S. Jagner, F. Soares-Carvalho, P. Thomas and J. P. Mercurio, *Better Ceramics through Chemistry VI (Mater. Res. Soc. Proc., Pittsburgh)*, 1994, **346**, 285; L. G. Hubert-Pfalzgraf, S. Parola, R. Papiernik, S. Jagner and J. P. Mercurio, 210th American Chemical Society Meeting, Chicago, 1995, INOR 039.
- 8 L. G. Hubert-Pfalzgraf, *Polyhedron*, 1994, **13**, 1181.
- 9 N. Ya. Turova, personal communication.
- 10 N. N. Sauer, E. Garcia and R. Ryan, *Mater. Res. Soc. Symp. Proc.*, 1990, **180**, 921.
- 11 S. C. James, N. C. Norman, A. G. Orpen, M. J. Quayle and U. Weckenmann, *J. Chem. Soc., Dalton Trans.*, 1996, 4159.
- 12 S. Daniele, L. G. Hubert-Pfalzgraf, J. C. Daran and S. Hault, *Polyhedron*, 1994, **13**, 927.
- 13 S. Boulmaaz, R. Papiernik, L. G. Hubert-Pfalzgraf, J. C. Daran and J. Vaissermann, *Chem. Mater.*, 1991, **3**, 779.
- 14 S. Boulmaaz, R. Papiernik, L. G. Hubert-Pfalzgraf and J. C. Daran, *Eur. J. Solid State Inorg. Chem.*, 1993, **30**, 583.
- 15 E. P. Turevskaya, D. V. Berdiev, N. Ya. Turova, Z. A. Starikova, A. I. Yanovsky, Y. T. Struchkov and A. I. Belokon, *Polyhedron*, 1997, **16**, 663.
- 16 W. J. Evans, T. J. Deming, J. M. Olofson and J. W. Ziller, *Inorg. Chem.*, 1989, **28**, 4027.
- 17 M. Veith, S. Mathur and V. Huch, *Inorg. Chem.*, 1997, **36**, 2391.
- 18 M. H. Chisholm, K. Foltling, J. C. Huffman and C. C. Kirkpatrick, *J. Chem. Soc., Chem. Commun.*, 1982, 189.
- 19 M. C. Massiani, R. Papiernik, L. G. Hubert-Pfalzgraf and J. C. Daran, *J. Chem. Soc., Chem. Commun.*, 1990, 301; *Polyhedron*, 1991, **10**, 437; M. A. Matchett, M. Y. Chiang and W. E. Buhro, *Inorg. Chem.*, 1990, **29**, 358.
- 20 C. M. Jones, M. D. Burkart and K. H. Whitmire, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 451.
- 21 F. Soares-Carvalho, P. Thomas, J. P. Mercurio, B. Frit and S. Parola, *J. Sol-Gel Sci. Technol.*, 1997, **8**, 759.
- 22 P. C. Joshi, A. Mansingh, M. N. Kamalasanan and S. Chandra, *Appl. Phys. Lett.*, 1991, **59**, 2389; N. Tohge, Y. Fuyuda and T. Minami, *Jpn. J. Appl. Phys., Part 1*, 1992, **31**, 4016; M. Toyoda, Y. Hamaji, K. Tomono and D. A. Payne, *Jpn. J. Appl. Phys., Part 1*, 1993, **32**, 4158.
- 23 M. Håkansson, Ph.D. Thesis, Chalmers University of Technology, Göteborg, 1990; *Inorg. Synth.*, in the press.
- 24 C. J. Gilmore, MITHRIL, *J. Appl. Crystallogr.*, 1984, 17.
- 25 TEXSAN-TEXRAY, Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985.

Received 24th July 1997; Paper 7/05365G