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Review

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# From molecules to bismuth oxide-based materials: Potential homo- and heterometallic precursors and model compounds

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# Abstract

Bismuth-containing heterometallic oxides are promising candidates for a variety of applications with respect to the microelectronics industry. This is not only because of their physical properties but also as a result of the environmentally benign nature of the bismuth-containing precursors and materials. Bismuth alkoxides, carboxylates and BiPh<sub>3</sub> have primarily been used as starting materials in the sol–gel and metal organic vapour deposition (MOCVD) process aimed at the preparation of bismuth oxide-based materials, whereas the interest in bismuth siloxides is more recent. Synthetic and structural aspects of these classes of compounds are discussed in this review. Bismuth alkoxides, siloxides and carboxylates hold potential as starting materials for more sophisticated heterometallic molecular precursors, which have to be developed in order to fully exploit the advantages of modern synthetic strategies that focus on µm and nm-scaled electronic devices and thin films. In this article molecular compounds with potential for the design of heterometallic bismuth oxide-based materials are presented together with feasible applications of the latter.

*Abbreviations:* acac, acetylacetonate; ALD, atomic layer deposition; BSS, bismuth subsalicylate; CMOS, complementary metal oxide semiconductor; CN, coordination number; Cp, cyclopentadienide; CVD, chemical vapour deposition; CSD, chemical solution deposition; DLI, direct liquid injection; DFT, density functional theory; EDS, energy dispersive spectrometry; EDTA, ethylenediamine tetraacetic acid; FRAM, ferroelectric random access memory; H<sub>2</sub>sal, salicylic acid; hfac, hexafluoroacetylacetonate; hmpa, hexamethyl phosphorous triamide; LI-MOCVD, liquid injection MOCVD; MOCVD, metal organic chemical vapour deposition; NVRAM, non-volatile random access memory; NBO, natural bond order; PLD, pulsed laser deposition; PVD, physical vapour deposition; *p*-tol, *para*-toluidine; sale, ethylenebis-salicylimine; salen', ethylenebis-3-methoxysalicylimine; SBT, strontium bismuth tantalate; SBTN, strontium bismuth tantalate; SBTN, strontium bismuth tantalate; SD410, Standard Oil of Ohio Company; SOFC, solid oxide fuel cell; SSP, single source precursor; tmhd, tetramethyleptanedione

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Additionally, a variety of structurally related high-nuclearity molecular bismuth oxo clusters are discussed that serve as model compounds, e.g. for the sol-gel process. The molecular structures of these metal oxo clusters provide insight into the stepwise formation of bismuth oxide following the hydrolysis/polycondensation route. The control over the growth process of metal oxo/hydroxo clusters is a key step in tailoring the morphology and physical properties of the final materials. Recent progress regarding various molecular architectures is presented. © 2006 Elsevier B.V. All rights reserved.

Keywords: Bismuth; Materials; CVD; Alkoxide; Siloxide; Carboxylate; Bismuth oxide; Cluster; C-H activation

# 1. Introduction

The continuing miniaturization of materials and devices for high-tech industrial applications is a challenge for scientists working in diverse fields of technology. Since the main focus of interest is the development of novel materials on the atomic, molecular and supramolecular level with typical dimensions on the nanometer scale, chemical research becomes of utmost importance in the fields of microelectronics and nanotechnology. A major challenge is the synthesis of well-defined nanomaterials of uniform size and morphology. Therefore a better knowledge of the aggregation and reaction sequences leading to a stepwise growth of nanoparticles starting from molecular precursors is necessary. The electronics industry offers an enormous market potential for nanomaterials and thus the widely used metal oxides are among the major targets of fundamental and applied research projects. Binary and ternary metal oxides exhibit the full spectrum of electronic, magnetic and optical properties including metallic, semiconducting, insulating, superconducting, ferroelectric, piezoelectric and ferromagnetic behaviour. Some of these properties might be combined within the same compound, giving access to multifunctional materials such as multiferroics. Recent development in the synthesis of metal oxide thin films and nanoparticles using chemical vapour deposition (CVD) techniques and solution based deposition techniques such as the sol-gel process even make the use of heteronuclear compounds and precursors of low volatility possible [1-6]. Thus chemically more complex systems are becoming available using established industrial processes. Key steps in the design of nanostructured metal oxide materials are the control of the chemical composition, the reactivity, the accessibility and the dimensions of the metal oxide surface.

Polynuclear metal oxo clusters serve as model compounds in order to gain a fundamental knowledge of the Aufbau principles of metal oxo(nano)clusters, and they might also hold potential as precursors for the synthesis of monodisperse nanoparticles. However, their practical use as precursors will be restricted to high-tech materials because metal oxo clusters often do not meet the criteria required for molecular precursors used on a large industrial scale. These criteria are: (i) simple, low-cost and high yield synthesis, (ii) high purity, (iii) simple handling, (iv) longterm storage without change of properties and (v) low toxicity. Additionally, depending on their application, the molecular precursors should show high volatility, high solubility or special reactivity. For the low-cost synthesis of homogeneous materials chemical reactions used for transformations such as thermolysis, hydrolysis and condensation should require mild reaction conditions.

Although nanomaterials are becoming more important, bulk metal oxide materials still dominate the industrial production. In this article various applications of the bulk bismuth oxidebased materials prepared via conventional and modern solid state syntheses are summarized. The scope is to demonstrate the potential of molecular precursors for the synthesis of bismuth oxide-based materials. It is not the aim to present a complete list of all precursors but to provide more detailed information about selected examples that have been published prior to spring 2006. The main emphasis is put on homo- and heterometallic bismuth alkoxides and silanolates of different complexity, which either hold potential as molecular precursors or as model compounds, whereby selected examples of heterometallic bismuth carboxylates are only briefly discussed. Additionally, attention is paid to the hydrolysis process of selected bismuth species. The structural characterization of bismuth oxo clusters that are formed upon partial hydrolysis provides insight into the formation of bismuth oxide and thus is of importance for the problem of how to control the formation of uniform metal oxide nanoparticles. Model compounds for the active bismuth sites in the heterogeneous oxidation process of propene over Bi<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub> to give acrolein are only briefly discussed. This latter topic was recently summarized by others [7,8].

# 1.1. Bismuth

Bismuth is one of those elements that in comparison to the lighter main group metals and metalloids has received relatively little attention in the past. However, bismuth compounds offer a broad spectrum of applications ranging from alloys and metallurgic additives via thermoelectric and ferroelectric materials to non-toxic pigments and catalysts, biocompatible additives in dental materials and remedies in human and veterinary medicine [9–12]. For example, (i) in the United States Pepto-Bismol<sup>®</sup> (BSS, bismuth subsalicylate) is an over the counter stomach remedy that is effective against upset stomach and diarrhoea [11,13]; (ii) various bismuth compounds represent alternatives for barium sulphate or zirconium compounds, which are used as radiopacifying additives to bone and dental cements [14–18]; (iii) so-called non-toxic yellow pigments on the basis of bismuth vanadate have been commercialised [19]; (iv) bismuth oxychloride is used in pigments for cosmetic products as artificial pearl; (v) bismuth triflate is among the most efficient and environmentally benign Lewis-acid catalysts [20]. An important driving force for the growing interest in these economically relevant applications of bismuth is the relatively low toxicity of bismuth compounds as compared to related species containing heavy metals such as Hg, Cd, Sn or Pb. Noteworthy, within group 15 antimony and arsenic compounds are generally of high toxic nature whereas those of bismuth exhibit a significantly reduced toxicity. In the future the toxicological aspect will become increasingly important for a variety of industries which on first sight do not significantly contribute to the pollution of the environment. One example is the growing microelectronics industry. Waste disposal of electronic devices will become a serious problem and environmentally benign materials are being sought. From this point of view bismuth-containing materials seem to be promising candidates, since the relatively low toxicity of the *metalloid* bismuth as compared with heavy metals is often stated. Nevertheless, the toxicological influence of bismuth and its compounds to the environment is still controversially discussed [21-29]. Detailed analyses are often scarce and only few compounds were systematically investigated. For example, it is well known that after exposure of humans to volatile BiMe3 or BiEt<sub>3</sub> irritation of the respiratory tract and conjunctive tissues occur; but these compounds are not stable under ambient conditions and are readily transformed to less toxic compounds of low solubility upon contact with air and/or moisture. On the other hand BiOCl and Ph<sub>3</sub>Bi are stable in air, they are classified non-toxic and neither show carcinogenic, mutagenic nor teratogenic effects. In conclusion, the data at hand do not allow a final environmental impact assessment.

With respect to physical properties that are important for the microelectronics technology multimetallic bismuth(III) oxides are a main target among bismuth-containing materials. They often show interesting physical properties as a result of the electronic and/or steric influence of the doubly occupied 6s orbital. For example, the ferroelectric properties of bismuth-containing perovskites [30–33], the electrooptical activity in sillenite-type compounds [34–42] and the multiferroic properties of ternary bismuth-containing oxides [43] are strongly influenced by the 6s lone pair. The latter causes strong distortions from ideal coordination geometries. Numerous examples of inorganic compounds demonstrate the unusual coordination chemistry of bismuth with coordination numbers in the range from 2 to 9. However, the exact nature of the stereochemical activity of the lone pair is still a point of controversial debate.

# 1.2. Bismuth oxide

The chemistry of the binary oxides of bismuth is dominated by the oxidation state +III. Reports on the synthesis and thermodynamic models of Bi<sub>2</sub>O<sub>5</sub> have occurred occasionally in the literature [44–48], but to the best of our knowledge only the mixed valent Bi(III,V) oxides Bi<sub>2</sub>O<sub>4</sub> [49] and Bi<sub>4</sub>O<sub>7</sub> [50] were characterized by X-ray crystallography. Bi<sub>2</sub>O<sub>5</sub> is stable only under high oxygen pressure. Stabilization of the highest oxidation state of bismuth is achieved in ternary metal oxides such as MBiO<sub>3</sub> (M = Li, Na, K, Ag) [51–54] and Li<sub>7</sub>BiO<sub>6</sub> [55]. Ternary mixed valent bismuthates such as Ag<sub>25</sub>Bi<sub>3</sub>O<sub>18</sub> [56,57], Ag<sub>2</sub>BiO<sub>3</sub> [58] and Ba<sub>2</sub>Bi<sub>2</sub>O<sub>6</sub> [59] were also prepared. In addition to mixed valent Bi(III)/Bi(V) compounds subvalent bismuth oxides such as BiO, Bi<sub>6</sub>O<sub>8</sub>, Bi<sub>7</sub>O<sub>8</sub> and Bi<sub>8</sub>O<sub>11</sub> have been reported [47,60–64]. However, most of the work on bismuth oxides concentrates on Bi<sub>2</sub>O<sub>3</sub>. The latter shows a distinctive



Scheme 1. Transformation temperatures for  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ - and  $\epsilon$ -Bi<sub>2</sub>O<sub>3</sub> [37, 65,66].

polymorphism including  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>,  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub>,  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> and recently characterized  $\varepsilon$ -Bi<sub>2</sub>O<sub>3</sub> (Scheme 1) [65,66]. Additionally, a metastable triclinic polymorph called  $\omega$ -Bi<sub>2</sub>O<sub>3</sub> was reported to occur at 800 °C on a BeO substrate. However, a structure model based on the X-ray diffraction data is not given [67]. Noteworthy, the  $Bi_2O_3$  polymorphs differ significantly in their electrical and optical attributes. The high temperature cubic phase, namely  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> [68], is among the most effective oxide ion conductors [69], but it is stable only between ca. 730 °C and its melting point at 824 °C [65,70-73]. The low temperature phase, namely  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>, is a p-type semiconductor. At 730 °C  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> transforms into the  $\delta$ -phase. On cooling a thermal hysteresis effect of the phase transition is observed if the sample was heated to a temperature above 750 °C prior to cooling. In this case the  $\delta$ -phase persists to a temperature of approximately 639–650 °C. It is also possible to stabilize  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> even at lower temperature by the addition of diverse metal cations in low concentration [74,75], but this is accompanied by a significant loss of its oxide ion conductivity compared with the pure  $\delta$ -phase [69,76]. Upon cooling a melt of bismuth oxide to a temperature of approximately 639–650 °C, δ-Bi<sub>2</sub>O<sub>3</sub> forms first, that might then transform into one of two metastable phases, namely either body centred cubic (b.c.c.)  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> or tetragonal  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> depending on the reaction conditions. The process is difficult to control and is strongly influenced by the presence of trace amounts of metal impurities and the texture of the sample. If the crystalline material is tempered at lower temperatures the thermodynamically stable  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> is expected to form. For example, the phase transformation from  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> was reported to occur in the temperature range 368-639 °C upon cooling, but  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> might also persist up to room temperature [65]. The thermal behaviour of bismuth(III) oxide is strongly affected by the amount and nature of the incorporated impurities, and on cooling large thermal hysteresis occurs. A synthetic protocol and a detailed structure analysis of y-Bi<sub>2</sub>O<sub>3</sub> using powder neutron diffraction was reported by Radaev et al. [37] They prepared  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> starting from  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> to which 0.1 mass% CdO was added prior to heating the ground sample in a platinum boat to 780 °C. This temperature was held for 4 h, than the sample was cooled down to  $400 \,^{\circ}$ C at a rate of  $1 \,^{\circ}$ C min<sup>-1</sup> and finally removed from the furnace. The  $\beta$ -phase is conveniently synthesized either by the decomposition of freshly prepared [(BiO)<sub>2</sub>CO<sub>3</sub>] through heating in air in an alumina boat at 377 °C for approximately 1.5 h [77] or by decomposition of bismuth oxalate under vacuum between 250 and 300 °C [78]. The novel polymorph  $\varepsilon$ -Bi<sub>2</sub>O<sub>3</sub> was obtained in low yield as a crystalline component of a mixture of phases including single crystals of  $\alpha$ - $Bi_2O_3$  upon hydrothermal treatment of  $Bi(NO_3)_3 \cdot 5H_2O$  in the presence of MnO<sub>2</sub>, MnSO<sub>4</sub>·H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> in a concentrated KOH solution [66]. EDS analysis of single crystals exclusively revealed the presence of bismuth and oxygen. Manganese and phosphorus were not detected and thus a mineralizing role was suggested for these elements because their presence is essential for the synthesis of orthorhombic  $\varepsilon$ -Bi<sub>2</sub>O<sub>3</sub>. Heating the latter polymorph to approximately 400  $^{\circ}$ C results in  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>. So far, much effort has been devoted to the phase-selective synthesis of bismuth oxide-based films (see Section 2.2), but recently studies on Bi2O3 nanoparticles, nanowires and nanotubes were also reported [79-83].

# 2. Synthesis and properties of bismuth oxide-based materials

# 2.1. Multimetallic oxides of bismuth

The potential for commercial applications of  $Bi_2O_3$  seems to be mainly restricted to sensors [84] and solid electrolytes [69]. In contrast, a broad spectrum of potential applications is offered by a variety of ternary and quaternary bismuthcontaining metal oxides. So far these materials have been demonstrated to be potentially useful as sensors, oxidation catalysts, pigments, superconductors, scintillators, photocatalysts, high temperature electrolytes and next generation data storage materials. In Table 1 different combinations of metals in multimetallic oxides are listed together with their properties, potential applications and methods of preparation. It is beyond the scope of this review article to give a detailed description of each heterometallic system. Instead, selected examples are briefly discussed in this section.

In addition to bismuth-containing superconductors [85,86], systems such as Bi/Ti/O and Bi/Sr/M/O (M=Nb, Ta) have received interest as ferroelectric materials and photocatalysts. Non-toxic pigments (Sicopal<sup>®</sup>) were prepared based on Bi/V/O, and metal oxides based on Bi/Mo/O are used as heterogeneous catalysts for the industrial production of acrolein and acrylonitrile. A recent review describes the role of bismuth in the SOHIO (Standard Oil of Ohio Company) process, which is the oxidation/ammoxidation of propene over bismuth/molybdate catalysts [8].

One of the main areas of interest with respect to heterometallic bismuth oxides is the development of novel ferroelectric materials, which are good candidates for non-volatile random access memories (NVRAM). Especially Aurivillius phases of the general type  $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$  (A = K, Sr, Ca, Pb, Bi; B = Ti, Zr, Nb, Ta, Mo, W, Fe, Co), which contain Bi<sub>2</sub>O<sub>2</sub>- layers, exhibit promising fatigue-resistant properties. Among these compounds the strontium bismuth tantalate (SBT), namely SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>, and strontium bismuth tantalate niobate (SBTN), namely SrBi<sub>2</sub>(Nb<sub>1-*x*</sub>Ta<sub>*x*</sub>)<sub>2</sub>O<sub>9</sub>, are among the most promising materials. They maintain adequate remnant polarization even after  $10^{12}$  switching cycles [33]. Lanthanum-substituted Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> shows similar performance and provides a promising alternative for ferroelectric random access memories (FRAM) [32,87,88].

A field of growing importance is a class of mixed metal oxide materials that is called multiferroics. These materials simultaneously show ferromagnetic, ferroelectric and/or ferroelastic long-range ordering. Coupling between the ferroelectric and the magnetic order parameters can lead to magnetoelectrical effects. Thus, the magnetization can be tuned by applying an electrical field and vice versa. Bismuth-containing compounds such as BiFeO<sub>3</sub> have emerged as very promising magnetoelectric multiferroic materials [43]. Noteworthy, the magnetization and the degree of magnetoelectric coupling seems to be size-dependent. High-quality thin films of BiFeO<sub>3</sub> show a polarization [43,89,90], which is distinct from that reported for the bulk material [91].

Most of the materials listed in Table 1 were first prepared by conventional solid state syntheses starting from the metal oxides or carbonates. This procedure is not a proper choice for the preparation of high-tech materials and devices with dimensions on the  $\mu$ m or even nm scale. More sophisticated syntheses such as the CVD technique and the sol-gel process are better suited for this purpose [92,93]. Both processes require milder reaction conditions than usually used for solid state reactions, and they allow for the synthesis of metastable phases. The recent developments in the sol-gel process and in the chemical vapour deposition used for the production of metal oxides make possible the use of more complex molecular precursors [1–4,94]. Processes such as liquid injection MOCVD (LI-MOCVD), chemical solution deposition (CSD), and atomic layer deposition (ALD) open up the use of novel molecular precursors for thin film preparation as well as for the construction of more complex devices. The sol-gel process is nowadays well established for the synthesis of a large variety of bismuth oxide-based materials [95–107]. In addition to mild reaction conditions it offers the aggregation of precursors on a molecular scale in terms of a preorganisation in advance of materials formation. Novel materials are easily accessible as a result of kinetically controlled reaction conditions. The use of molecular bismuth precursors in MOCVD is more recent, but thin film preparation of bismuth oxide-based materials is of growing interest.

## 2.2. Synthesis of bismuth oxide-based thin films

The synthesis of uniform  $Bi_2O_3$  films is impeded by the formation of non-stoichiometric subvalent  $Bi_xO_y$  phases. On the other hand, the formation of mixed valent Bi(III,V) compounds such as  $Bi_2O_4$  [49] or  $Bi_4O_7$  [50] seems to be negligible for the preparation of thin bismuth oxide films even under oxidising conditions. However, using the electrodeposition method the formation of  $\delta$ - $Bi_2O_3$  single crystals on a Au substrate was pro-

Table 1
Selected examples of heterometallic bismuth oxides

Compound	Sunthasia	Droporty	Application	Litoratura
	Synthesis	riopeny	Application	Literature
Bi–Ti–O				
Bi <sub>2</sub> TiO <sub>7</sub>	Sol-gel	Dielectric	Data storage media (DRAM)	[108]
Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>	Sol–gel, CVD, ALD, solid state reaction, pyrolysis,	Ferroelectric	Data storage media (FRAM)	[99,100,109–116]
$Bi_{4-x}Ln_xTi_3O_{12}$ (Ln = La, Nd)	SSP-pyrolysis, etc. Sol–gel, solid state reaction, MOCVD	Ferroelectric	Data storage media (FRAM)	[32,117–134]
Bi <sub>12</sub> TiO <sub>20</sub>	Solid state reaction	Electrooptically active, piezoelectric, photoelectric	Holographic data storage media, electrooptical modulators	[42,135–139]
Na <sub>0.5</sub> Bi <sub>0.5</sub> TiO <sub>3</sub>	Sol-gel, solid state reaction	Ferroelectric, piezoelectric	Data storage media	[140–144]
Bi-Mo-O				
$Bi_2O_3 \cdot nMoO_3 \ (n = 1-3)$	Sol–gel, SSP-pyrolysis, solid state reaction, spray-pyrolysis, etc.	Photoelectric, oxygen ion conducting	Oxidation catalyst, sensor, SOFC	[7,145–153]
Bi–W–O	I SIS SUBTI			
Bi <sub>2</sub> WO <sub>6</sub>	Solid state reaction	Ferroelectric	_a	[152,154–159]
Bi–V–O				
BiVO <sub>4</sub>	Sol–gel, SSP-pyrolysis, solid state reaction	Photoelectric, oxygen ion conducting	Photocatalyst, pigment	[160–168]
$Bi_4V_2O_{11}/Bi_2M_xV_{1-x}O_{5.5-\delta}$ (M = diverse metals)	Solid state reaction, sol-gel, MOCVD, thermolysis of hybrid materials, SSP-pyrolysis	Dielectric, pyroelectric, ferroelectric, oxygen ion conducting (γ-phase)	Solid elctrolyte, SOFC, membrane, lithium ion batteries, catalyst, gas sensor	[106,162,169–181]
Bi–Fe–O	1.5			
BiFeO <sub>3</sub>	Sol–gel, solid state reaction, PLD	Ferroelectric,ferro- magnetic, ferroelastic, piezoelectric	Magnetic data storage media, gas sensor	[43,89–91,182–197]
Bi <sub>2</sub> Fe <sub>4</sub> O <sub>9</sub>	Solid state reaction	Anti-ferromagnetic	Gas sensor, catalyst	[183,198–201]
Bi-Mn-O				
BiMnO <sub>3</sub>	Solid state reaction, spray-pyrolysis	Ferroelectric, ferromagnetic	Data storage media	[202–206]
Bi-Sn-O				
$Bi_2Sn_2O_7$	Spray-pyrolysis, solid state reaction	Semiconducting	Catalysts, gas sensor	[207–213]
Bi-M-O(M = Ge, Si)				
$Bi_4M_3O_{12}$	Solid state and hydro-thermal synthesis, sol-gel, CVD	Electrooptically active, luminescent	Scintillator, data storage media	[214–220]
$\begin{array}{l} \operatorname{Bi}_{2-x}\operatorname{Ln}_{x}\operatorname{GeO_{5}}\left(\operatorname{Ln}=\operatorname{Y},\operatorname{Yb}\right)\\ \operatorname{Bi}_{12}\operatorname{MO_{20}}\end{array}$	Solid state reaction Solid state reaction, sol-gel, pulsed laser deposition, plasma sputtering	Luminescent Optically active, photorefractive, photoelectric, electrooptical active	Laser, optical amplifier Optical data storage, optics	[221] [35,36,38-42,222-233]
Bi <sub>12</sub> SiO <sub>20</sub> :Nd	Solid state reaction	Luminescent	Laser	[234–236]
Bi–Ba–O				
BaBiO <sub>3</sub> Ba <sub>0.6</sub> K <sub>0.4</sub> BiO <sub>3</sub>	Solid state reaction Solid state reaction	Semiconducting Supraconducting	<sup>_a</sup> Superconductor	[59,237] [238,239]
P: V O		. 0	*	
$Bi_2O_3 - Y_2O_3$	Solid state reaction	Oxygen ion conducting	Solid electrolyte	[69,240–243]
Bi-M-O (M = Ta, Nb) $BiMO_4$	Solid state reaction,	Antiferroelectric,	Data storage media	[244–248]
$BiTa_{1-x}Nb_xO_4$	Solid state reaction	Photoelectric	Photocatalyst	[249]
Bi-M-O				
$BiMO_3$ (M = Al, Ga, Sc, Co, Ni, Cr)	Solid state reaction	_a	_a	[250–256]
Bi–Sr–Ca–Cu–O Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>n</sub> O <sub>x</sub> $(n = 2, 3)$	Solid state reaction, sol-gel	Supraconducting	Superconductor	[257–259]

Tab	le 1	(Continued)	)

Compound	Synthesis	Property	Application	Literature
Bi-Sr-M-O(M = Ta, Nb)				
Bi <sub>2</sub> SrTa <sub>2</sub> O <sub>9</sub>	Sol-gel, CVD, PLD, ALD	Ferroelectric	Data storage media (FRAM)	[33,97,98,101,102,107, 260–278]
Bi <sub>2</sub> SrNb <sub>2</sub> O <sub>9</sub>	Sol–gel, CVD, co-precipitation, pulsed laser ablation	Ferroelectric	Data storage media (FRAM)	[105,279–295]
$Bi_2Sr(Ta_{2-x}Nb_x)_2O_9$	Sol-gel, solid state reaction	Ferroelectric	Data storage media (FRAM)	[33,260,261,296,297]
Bi–Ln–Ru–O				
$Bi_{2-y}Ln_yRu_2O_7$	Solid state reaction	Semiconducting/conducting	_a	[298–301]
Pb-Bi-Nb-O				
PbBi <sub>2</sub> Nb <sub>2</sub> O <sub>9</sub>	Solid state reaction	Photoconducting	Photocatalyst	[302]

Synthesis, selected properties and potential applications.

<sup>a</sup> Not specified.

<sup>b</sup> Thin films.

posed to follow a reaction pathway, in which Bi(V) oxide was postulated to occur as an intermediate [303].

The preparation of bismuth oxide films was achieved through different techniques such as oxidation of bismuth films [304-309], evaporation of bismuth in an atmosphere of oxygen [310,311], electrodeposition [303,312], PVDtechniques [304,313,314] sol-gel process [96,218], and CVD techniques such as metal-organic vapour deposition (MOCVD) [260,315–317], liquid injection CVD [318,319] and atomic layer deposition (ALD) [262]. In addition to the problem of the formation of non-stoichiometric bismuth oxide phases, the high reactivity of molten bismuth oxide causes great difficulties for the production of films with reproducible physical properties. In the melt bismuth oxide reacts with almost all crucible materials except platinum. Thus thin film formation of bismuth oxide must proceed significantly below the melting temperature of 824 °C. The most promising approaches with respect to control of reproducibility, uniformity of the final material, composition, and compatibility with modern silicon-based CMOS technologies are based on CVD techniques. Therefore a number of volatile molecular precursors have been studied with respect to their potential for the deposition of either homo- or heterometallic bismuth oxide films. These studies include diverse compounds such as bismuth halides [110,320–322], BiPh<sub>3</sub> [111,169,219b,269,315,316,323–336], Bi(o-C7H8)3 BiMe<sub>3</sub> [260.274.317.338-340]. [337]. [Bi(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>] [341],  $[Bi(CH_2CH=CH_2)_3]$ [263],  $[Bi(tmhd)_3]$  (tmhd = tetramethylheptanedione) [319,324,330], [262],  $[Bi{N(SiMe_3)_2}_3]$  $[Bi(OCMe_2Et)_3]$  [342], and [Bi(OCMe<sub>2</sub>CH<sub>2</sub>OMe)<sub>3</sub>] [261,318,343,344]. The use of bismuth alkoxides [Bi(OR)<sub>3</sub>] offers some advantages such as a clean decomposition process as was shown for [Bi(OCMe<sub>2</sub>CH<sub>2</sub>OMe)<sub>3</sub>]. A low carbon contamination of the final material and control of solubility and volatility by the choice of the alkoxide ligand constitute additional advantages. In contrast, bismuth halides tend to give bismuth oxyhalides in the presence of H<sub>2</sub>O and liberate hydrogen halides [110], [Bi(tmhd)<sub>3</sub>] is not compatible with Sr-Ta(Nb) alkoxides [2], volatile trialkyl bismuth compounds such as Me<sub>3</sub>Bi are potentially harmful [1,10], [Bi(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>] gives bismuth silicates [341], and the decomposition of triaryl bismuth compounds to give a single phase is difficult to control and requires the addition of an additional oxygen source [315,316].

The alkoxides [Bi(OCMe<sub>2</sub>CH<sub>2</sub>OMe)<sub>3</sub>] and [Bi(OCMe<sub>2</sub>Et)<sub>3</sub>] as well as the amide  $[Bi{N(SiMe_3)_2}_3]$  were shown to be suitable for the synthesis of Bi-Ta-O and Sr-Bi-Ta-O films, but their usage as CVD precursors requires a DLI (direct liquid injection) system [262,318,329]. Simple bismuth alkoxides  $[Bi(OR)_3]$  (R = Me, Et, *i*Pr) have been reported previously [345] and the application of [Bi(OEt)<sub>3</sub>] for the synthesis of Bicontaining high-T<sub>c</sub> superconductors using MOCVD was briefly reported in a communication [346]. However, moderate solubility and poor volatility of [Bi(OR)<sub>3</sub>] (R = Me, Et, *i*Pr) limit their practical use as precursors for CVD applications. In contrast, the sterically more demanding [Bi(OtBu)<sub>3</sub>] is accessible in high vield, is non-toxic, moderately soluble in common organic solvents, volatile and can be handled without decomposition under inert atmosphere.  $[Bi(OtBu)_3]$  was not investigated as precursor for the deposition of bismuth oxide thin films by MOCVD until recently, although its potential use for the preparation of superconducting materials was suggested [1,2,318]. Indeed  $[Bi(OtBu)_3]$  is well suited for the phase-selective deposition of thin bismuth oxide films [347].

Bismuth siloxides of the type  $[Bi(OSiR_3)_3]$  represent another class of compounds with potential for the preparation of thin films of bismuth oxide or bismuth silicates. It might be expected that bismuth siloxides eliminate R<sub>3</sub>SiOSiR<sub>3</sub> upon thermally induced decomposition to give Bi<sub>2</sub>O<sub>3</sub>. This process should be favoured over the elimination of a silaethene R<sub>2</sub>Si=CH<sub>2</sub> to give Bi-OH in the first reaction step followed by a condensation reaction to give the parent bismuth oxide. However, preliminary experiments have shown that thin films produced by spin-coating of  $[Bi(OSiR_3)_3]$  followed by thermal treatment tend to give bismuth silicates instead of pure Bi<sub>2</sub>O<sub>3</sub> [348]. This behaviour is explained by the easy formation of the sillenite type compound Bi<sub>12</sub>SiO<sub>20</sub>, which readily forms and crystallizes even under mild reaction conditions [36,38]. Thus, silicon contamination must be completely excluded during thermal decomposition of bismuth siloxides in order to prepare pure bismuth oxide.

## 3. Homometallic precursors and model compounds

### 3.1. Bismuth alkoxides

Homoleptic metal alkoxides are among the most important starting compounds for the synthesis of bismuth oxidecontaining materials prepared by the CVD or the sol-gel process. However, until two decades ago reports on bismuth alkoxides were scarce. This situation has changed since and several bismuth alkoxides and aryloxides have been prepared and structurally characterized. In Table 2 a list of these compounds together with the synthetic methods used for their preparation and the techniques used for their characterization is given. Several synthetic approaches have been proposed, which show a large range of yields. Although no detailed study on the factors that influence the yields is available, the success of the synthetic method seems to depend strongly on the organic substituent R (Scheme 2). The methods reported include metathesis (A), alcohol-amine exchange (B), alcohol-alcohol exchange (C), benzene elimination starting from BiPh<sub>3</sub> and alcohols (D), electrochemical oxidation (E) and alcoholysis of freshly prepared bismuth hydroxide (F) (see Scheme 2 and Table 2).

The conventional metathesis route A has been the method of choice for the synthesis of most of the bismuth alkoxides of the type [Bi(OR)<sub>3</sub>] (R = Me, Et, *i*Pr, *t*Bu, CH(CF<sub>3</sub>)<sub>2</sub>, OCPh<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>OMe). Yields in the range from almost quantitative to very low have been reported. Bismuth aryloxides such as [Bi(OC<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>)<sub>3</sub>] and [Bi(OC<sub>6</sub>Cl<sub>5</sub>)<sub>3</sub>] were also prepared by salt elimination, but this method failed when using the phenolate derivatives NaOC<sub>6</sub>H<sub>2</sub>-2,4,6-(CF<sub>3</sub>)<sub>3</sub>, NaOC<sub>6</sub>H<sub>3</sub>-2,6-*i*Pr<sub>2</sub> or NaOC<sub>6</sub>F<sub>5</sub> in THF [8,349,350]. For example, the metathesis reaction between BiCl<sub>3</sub> and NaOC<sub>6</sub>F<sub>5</sub> carried out in THF



Scheme 2. Methods used for the synthesis of bismuth alkoxides.

did not give  $[Bi(OC_6F_5)_3]$  but homo- and heterometallic bismuth oxo clusters were isolated instead (see Section 3.3) [349]. These metal oxo clusters may result from microhydrolysis, but Bi–O–M (M=Bi, Na) bond formation was also observed as a result of ether elimination. The choice of the solvent has a significant influence on the outcome of the metathesis reaction. Whereas  $[Bi(OC_6F_5)_3]$  was not isolated from THF, its synthesis was possible in toluene [349]. The presence of sodium cations promotes the formation of the metal oxo clusters with elimination of the corresponding ether. The latter process is facilitated by the use of polar solvents and is even more significant for bismuth siloxides (see Section 3.2). However, in some cases the Bi–O–Bi bond formation with elimination of an ether or a siloxane is also

Table 2

Synthesis and characterization of homoleptic bismuth alkoxides and aryloxides

Compound	Synthesis	Analyses	Literature
[Bi(OMe) <sub>3</sub> ]	A, C, E	IR, MS	[345,367]
[Bi(OEt) <sub>3</sub> ]	А	IR, MS	[345,364,367,380]
$[Bi(OEt)_3] \cdot (7 + x) EtOH$	А	XRD	[370]
[Bi(OiPr) <sub>3</sub> ]	A, B, E	IR, MS	[342,345,367]
[Bi(OtBu) <sub>3</sub> ]	А	<sup>1</sup> H, <sup>13</sup> C NMR, IR, MS, gas phase electron diffraction	[351,363,364,371,372]
[Bi(OCMe <sub>2</sub> Et) <sub>3</sub> ]	В	<sup>1</sup> H NMR	[342]
$[Bi(OCH_2CMe_3)_3(L)], L = HOCH_2CMe_3, pyridine$	В	<sup>1</sup> H NMR, IR, XRD	[362]
$[Bi{OCH(CF_3)_2}_3(thf)_2]$	А	<sup>1</sup> H, <sup>19</sup> F NMR, IR, XRD	[373]
[Bi(OCH <sub>2</sub> CH <sub>2</sub> OMe) <sub>3</sub> ]	В	<sup>1</sup> H, <sup>13</sup> C NMR, IR, MS, XRD	[342,363,364]
$[Bi_4(OCH_2CH_2OH)_2 (OCH_2CH_2O)_5]$	F	IR	[381a]
[Bi <sub>2</sub> (OCH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> ]	F	XRD	[381b]
[Bi(OCMe <sub>2</sub> CH <sub>2</sub> OMe) <sub>3</sub> ]	A, B	<sup>1</sup> H, <sup>13</sup> C NMR, IR, MS, XRD	[318,343]
[Bi(OCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> ) <sub>3</sub> ]	В	<sup>1</sup> H NMR	[342]
[Bi(OCHMeCH <sub>2</sub> NMe <sub>2</sub> ) <sub>3</sub> ]	В	<sup>1</sup> H NMR	[342]
[Bi(OCPh <sub>3</sub> ) <sub>3</sub> ]	А	<sup>1</sup> H, <sup>13</sup> C NMR, IR, XRD	[382]
[Bi(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N]	F	<sup>1</sup> H NMR, XRD	[369]
$[EtOBi{C_5H_3N-2,6-(CEt_2O)_2}]$	С	<sup>1</sup> H, <sup>13</sup> C NMR, XRD	[366]
$[Bi(OC_6H_3Me_2-2,6)_3]$	А	<sup>1</sup> H NMR, IR, XRD	[371]
$[Bi(OC_6F_5)_3]$ solvate (toluene, THF and hexane)	A, D	<sup>19</sup> F NMR, IR, XRD	[349,357,373]
$[Bi(OC_6Cl_5)_3]$	А	-	[349]
[Bi(OC <sub>6</sub> H <sub>3</sub> -2,6- <i>i</i> Pr <sub>2</sub> ) <sub>3</sub> ]	В	XRD	[365]



Fig. 1. Molecular structure of  $[Bi_6O_3(OAr)_{12}]$  (Ar = C<sub>6</sub>H<sub>3</sub>-2,6-Cl<sub>2</sub>) [355]. Bismuth and carbon atoms as well as Bi–O bonds are given in black, while O and Cl atoms are represented by different shades of grey from brighter to darker.

observed in less polar solvents such as benzene or toluene at higher reaction temperatures [351,352]. It is interesting to note that the presence of sodium cations not only facilitates ether formation but also favours the crystallization of heterobimetallic species. The similar ionic radii of Na<sup>+</sup> and Bi<sup>3+</sup> in combination with their unspecific and variable coordination chemistry allow the easy formation of sodium-bismuth (oxo)alkoxides and (oxo)aryloxides [349,351,353]. The tendency to form heterobimetallic complexes with lithium or potassium is reduced compared with sodium but cannot be excluded completely [351,354].

Whitmire et al. reported an elegant alternative method for the preparation of  $[Bi(OC_6F_5)_3]$  [349]. The latter compound was isolated in high yield by the reaction of BiPh<sub>3</sub> and pentafluorophenol in CH<sub>2</sub>Cl<sub>2</sub> or toluene. Noteworthy, triphenylbismuth is commercially available and can be stored without decomposition even in the presence of moisture, thus making it an appropriate precursor. Another example of a Bi-Ph bond cleavage was reported for the reaction of BiPh<sub>3</sub> with 2,6-dichlorophenol in toluene at reflux. However, [Bi(OC<sub>6</sub>H<sub>3</sub>-2,6-Cl<sub>2</sub>)<sub>3</sub>] was not isolated from the reaction mixture (Eq. (1)). Instead the homometallic bismuth oxo cluster  $[Bi_6O_3(OAr)_{12}]$  (Ar = C<sub>6</sub>H<sub>3</sub>-2,6-Cl<sub>2</sub>) was obtained and characterized by a single crystal X-ray structure analysis (Fig. 1) [355]. The origin of the oxo ligand is most likely the result of partial hydrolysis from trace amounts of water rather than of ether elimination although the latter process cannot be ruled out completely. Similarly, hydrolysis of the Bi-C bond followed by a condensation reaction was observed for the benzoxabismole RBi( $C_6H_4$ -4-CH<sub>3</sub>) (R =  $-C_6H_3$ -5-C(CH<sub>3</sub>)<sub>3</sub>-2- $C(CF_3)_2O_{-}$ ). The resulting dibismuth oxo alkoxide [RBiOBiR]<sub>2</sub> is dimeric in the solid state and adopts a ladder-like arrangement of Bi and O atoms [356]. Althoung these results demonstrate the principle application of the synthetic method D, the solvolytic cleavage seems to be of limited synthetic utility. Compounds such as 1,1,1,3,3,3-hexafluoro-2-propanol and pentachlorophenol failed to react with BiPh<sub>3</sub> [349,357].



Attempts have been reported to extend the acid–base reaction strategy using an organometallic bismuth compound and an acidic E–OH group to other systems. It was shown that the reaction of triphenyl bismuth with  $tBuPh_2SiOH$  provides the corresponding bismuth siloxide [Bi(OSiPh\_2tBu)\_3], but only with moderate yield and after prolonged reaction time [358]. Replacing BiPh<sub>3</sub> by the benzyl derivative [Bi(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-Cl-2)<sub>3</sub>] was not successful and gave elemental bismuth and a mixture of products which have not been further characterized [359]. The reaction of Et<sub>3</sub>Bi with HOC<sub>6</sub>F<sub>5</sub> or HOC<sub>6</sub>H<sub>5</sub> gave monosubstituted compounds (Eq. (2)) [360].



Even by the use of an excess of the phenol derivative heteroleptic compounds instead of the homoleptic bismuth aryloxides were isolated. In the solid state the heteroleptic compounds both form a coordination polymer with tetracoordinate bismuth atoms and bridging aryloxide ligands (Fig. 2). As a result of a crystallographic three-fold screw axis, helical chains are formed. The coordination geometry at the bismuth atom might be described as a pseudo pentagonal bipyramid with the lone pair occupying an equatorial position. The Bi–O bond lengths amount to 2.411 Å in Et<sub>2</sub>BiOC<sub>6</sub>F<sub>5</sub> and 2.382 Å in Et<sub>2</sub>BiOC<sub>6</sub>H<sub>5</sub>,



Fig. 2. Graphical representation of the chiral coordination polymer  $[Et_2BiOC_6F_5]_n$  [360].

which is intermediate between typical bond lengths for primary and secondary Bi–O bonds and thus might be interpreted as hypervalency. Noteworthy, the first report on a diorganobismuth alkoxide, namely  $Et_2BiOEt$ , dates back to 1942 [361], but structural data were not available at that time.

Another approach to circumvent the problems observed with the metathesis reaction A is the alcohol/amine exchange using  $[Bi(NMe_2)_3]$  or  $[Bi\{N(SiMe_3)_2\}_3]$ . Similar to the reaction of an alcohol with BiPh<sub>3</sub>, this reaction is classified as an acid–base reaction. The method is more general and was shown to give bismuth alkoxides in high yields [342,343,362–365]. However, it should be kept in mind that the bismuth amide must first be prepared by a metathesis reaction starting from BiCl<sub>3</sub> and the corresponding sodium amide and that the bismuth amide is sensitive towards moisture.

The alcohol exchange reaction C should be applicable to a large range of bismuth alkoxides, but it has been scarcely used so far. One example is the synthesis of the heteroleptic bismuth alkoxide bearing a pyridinedimethoxide ligand from in situ prepared [Bi(OEt)<sub>3</sub>] [366]. The reaction is given in Eq. (3). In addition to the intramolecularly coordinated bismuth alkoxide [EtOBi{C<sub>5</sub>H<sub>3</sub>N-2,6-(CEt<sub>2</sub>O)<sub>2</sub>}] several related monoorganobismuth compounds of the formula [RBi{C<sub>5</sub>H<sub>3</sub>N-2, 6-(CR'<sub>2</sub>O)<sub>2</sub>}] (R=Me, Ph; R'=Me, Et) have been reported [366].



A second example for the synthesis method C is the preparation of bismuth methoxide [Bi(OMe)<sub>3</sub>] starting from [Bi(OEt)<sub>3</sub>] and methanol [367]. The insoluble bismuth methoxide is conveniently obtained either by the reaction of methanol with solid [Bi(OEt)<sub>3</sub>] or from an ethanolic solution of the latter. It is crucial to use carefully dried solvents, because in the presence of water [BiOOMe] is expected to form. The bismuth oxo methoxide [BiOOMe] is accessible with high yields starting from  $[BiO(NO_3)]$ ,  $[Bi(NO_3)_3]$ ,  $[Bi(ClO_4)_3]$  or  $[Bi(OOCC_6H_4-$ OH-2)<sub>3</sub>] and NaOH in methanol [368]. In this regard the results reported by Bachman et al. about the synthesis of [Bi(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N] following route F are somewhat surprising [369]. Freshly prepared "Bi(OH)3" was reacted in ethanol to which sodium and triethanolamine had been added. After the solution had been diluted with methanol the bismuth alkoxide [Bi(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N] precipitated. The freshly prepared bismuth hydroxide, which is presumably the bismuth oxo hydroxide, was prepared from bismuth nitrate in dilute nitric acid after addition of an aqueous solution of NaOH. Obviously, the multidentate ligand favours the formation of a bismuth alkoxide over an oxo

alkoxide and renders the product more stable towards hydrolysis. Molecular bismuth alkoxides which are not stabilized by intramolecular coordination or steric effects are much more sensitive towards water or even moisture.

Kucheiko et al. have shown that bismuth alkoxides are accessible via anodic oxidation of the metal in a medium of the absolute alcohol to which had been added  $[Bu_4N]Br$  as electrolyte. Although it was shown that the synthetic method E is in principle applicable to both  $[Bi(OMe)_3]$  and  $[Bi(OiPr)_3]$ , it was recommended only for the synthesis of the methoxide derivative. It was assumed that in the case of *i*PrOH the bismuth alkoxide forms as well, but reduction of  $[Bi(OiPr)_3]$  at the cathode to give the metal was observed. For bismuth methoxide this secondary process can be neglected as a result of its low solubility.

The simple bismuth alkoxides  $[Bi(OR)_3]$  (R = Me, Et, iPr) have been prepared first by Mehrotra and Rai as early as 1966 using the conventional metathesis route A [345]. These simple bismuth alkoxides are not well suited as precursors for materials synthesis due to their low solubility and poor volatility. Although their molecular structures in the solid state have not been determined so far, it is expected that polymeric complexes are formed in which the bismuth atoms are connected through µalkoxide ligands. This hypothesis is not supported by the solid state structure of the bismuth ethoxide ethanol solvate [370]. The compound was prepared by the metathesis route A, and single crystals have been isolated from an ethanol solution with 95% yield. The compound analysed to  $[Bi(OEt)_3]_8 \cdot (7 + x) EtOH$ . The single crystal X-ray diffraction analysis reveals the formula [Bi(OEt)<sub>3</sub>]<sub>8</sub>·7EtOH with seven bismuth atoms being hexacoordinate and one being pentacoordinate as long as only Bi-O bond lengths shorter than 3.0 Å are taken into account. Each bismuth atom is bridged through two  $\mu$ -ethoxide ligands to give an octanuclear ring structure with a crown shape (Fig. 3). Thus it seems to be likely, that the simple bismuth alkoxides  $[Bi(OR)_3]$ adopt oligomeric structures, although polymeric complexes cannot be excluded for the solvate-free derivatives.

The substitution of an *iso*-propoxy group in  $[Bi(OiPr)_3]$  by the acetylacetonate anion (acac) significantly enhances the solubility in polar solvents such as THF [100]. The resulting product  $[Bi(OiPr)_2(acac)]$  is best described as a centrosymmetric dimer in the solid state with Bi–OiPr bond lengths of 2.12, 2.20 and 2.50 Å (Fig. 4). It further aggregates through secondary bonds to give a one-dimensional polymer (Bi–O 2.69 Å). Possibly,  $[Bi(OiPr)_2(acac)]$  is dimeric in THF solution. Similarly,  $[Bi(OCH_2CH_2OMe)_3]$  was reported to adopt a dimeric molecular structure, which upon further Bi–O coordination results in a polymeric chain structure in the solid state [342,363].

The solubility as well as the volatility of  $[Bi(OtBu)_3]$  are increased compared with the sterically less demanding bismuth alkoxides  $[Bi(OR)_3]$  (R = Me, Et, *i*Pr). The former compound is easily prepared by the metathesis route A using either BiCl<sub>3</sub> or BiBr<sub>3</sub> and sodium or potassium *tert*-butoxide. Its synthesis was independently developed by Evans et al. [371] and Hubert-Pfalzgraf and coworkers [363], but neither group was able to determine the molecular structure in the solid state. This is even more surprising, since  $[Bi(OtBu)_3]$  can be easily crystallized from various solvents. Single crystals which were



Fig. 3. Bismuth–oxygen core structure of  $[Bi(OEt)_3]_8$ ·7EtOH [370]. The Bi–O bond lengths are in the range of 2.0–3.0 Å. Carbon and hydrogen atoms are omitted. The black spheres correspond to bismuth atoms and the grey spheres to oxygen atoms.

grown from hexane at low temperature were studied by X-ray diffraction analyses, but the structure could not be completely solved and refined. The setting was reported to be hexagonal with a = b = 16.9065(28) Å and c = 9.5398(33) Å. It was assumed that the compound is monomeric in the solid state, but so far a



Fig. 4. . Cut-out of the one-dimensional chain structure of  $[Bi(OiPr)_2(acac)]$ [100]. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while O atoms are represented by grey spheres. Bond lengths are given in Å.



Fig. 5. Graphical representation of the molecular structure of  $[Bi(OCMe_2-CH_2OMe)_3]$  in the solid state [318,343].

straightforward evidence is lacking [371]. We did observe similar results for single crystals grown from pentane and toluene [359], but the molecular structure in the solid state still remains to be elucidated. In contrast the molecular structure in the gas phase was studied by Haaland et al. using gas electron diffraction [372]. [Bi(OtBu)<sub>3</sub>] was shown to be monomeric with a bismuth-oxygen bond length of 2.067(4) Å and O-Bi-O bond angles of 90(1)°. Despite the high volatility of  $[Bi(OtBu)_3]$  and the interest in volatile bismuth compounds as precursors used in MOCVD of electroceramic oxides, to the best of our knowledge its application in MOCVD had not been reported until recently [347]. This lack of investigation of  $[Bi(OtBu)_3]$  might be attributed to reports, in which it is stated that the bismuth tertbutoxide is highly air sensitive and has only limited stability in solution [2,318]. Indeed, partial hydrolysis of [Bi(OtBu)<sub>3</sub>] in solution was reported to give [Bi<sub>4</sub>O<sub>2</sub>(OtBu)<sub>8</sub>] [365], but if carefully handled under anaerobic conditions we did not observe noticeable decomposition after prolonged storage. Its promising evaporation characteristics prompted us to use  $[Bi(OtBu)_3]$ for MOCVD of thin Bi<sub>2</sub>O<sub>3</sub> films and we were able to deposit phase selectively the  $\alpha$ -,  $\beta$ - and  $\gamma$ -phase [347].

Following the concept of intramolecular donor stabilization, in 1993 Herrmann et al. have reported the synthesis of  $[Bi(OCMe_2CH_2OMe)_3]$  (Fig. 5) [343]. They have proposed that the bismuth alkoxide should be well suited for materials synthesis as a result of its high solubility and volatility. However, the proposed molecular structure was confirmed only in 2001 by Williams et al. using single crystal X-ray diffraction analysis [318]. This group also demonstrated the high potential of  $[Bi(OCMe_2CH_2OMe)_3]$  for the synthesis of thin bismuth oxide films, verifying the earlier hypothesis.

It is well known that the volatility of molecular precursors is significantly enhanced by the introduction of C–F bonds. Within the family of bismuth alkoxides this is nicely demonstrated by a comparison of the physical properties of  $[Bi\{OCH(CH_3)_2\}_3]$  [345] and  $[Bi\{OCH(CF_3)_2\}_3]$  [357]. Whereas the former alkoxide is almost insoluble in all common organic solvents and sublimes only with low yield at 140 °C (10<sup>-3</sup> Torr), the fluorinated compound can be easily dissolved in aromatic solvents and THF, and it readily sublimes at 100 °C (10<sup>-3</sup> Torr). However, thermolysis of  $[Bi\{OCH(CF_3)_2\}_3]$  under an inert atmosphere gave predominantly BiOF instead of the pure oxide. The high volatility is attributed to the dimeric nature of  $[Bi\{OCH(CF_3)_2\}_3]$  in the solid state. The fluorinated compound crystallizes from



Fig. 6. Molecular structure of  $[Bi{OCH(CF_3)_2}_3thf]_2$  [357]. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while O and F atoms are represented by different shades of grey from brighter to darker, respectively.

THF in form of its dimeric thf-adduct [Bi{OCH(CF<sub>3</sub>)<sub>2</sub>}<sub>3</sub>thf]<sub>2</sub> with two bridging fluoroalkoxide ligands (Fig. 6) [373]. The bismuth atoms are pentacoordinate with a coordination geometry that might be described as square pyramidal or pseudooctahedral with a stereochemically active lone pair occupying one octahedral site. However, there is still some debate about the stereochemical activity of the lone pair at bismuth. In some compounds as for instance in  $[Bi{OCH(CF_3)_2}_3]$  the bismuth atom adopts a configuration in which the lone pair appears to be stereochemically active and in others it does not. This puzzling structural coordination chemistry has not been fully clarified so far. With regard to this discussion the molecular structures of  $[Bi{OCH(CF_3)_2}_3thf]_2$ ,  $[Bi(OC_6F_5)_3(thf)_2]_2$ and  $[Bi(OC_6F_5)_3(toluene)]_2$  reveal some interesting structural aspects (Figs. 6-8). These compounds feature the same basic structural characteristics, i.e. a dimeric structure with two asymmetrically bridging alkoxide ligands and additional vacant coordination sites that are fully or partly occupied by solvent molecules. Noteworthy, the coordination of arene ligands to a bismuth atom is a well known phenomenon and was reported for a large variety of Lewis-acidic bismuth compounds [358,373–379].

If the lone pair is assumed to be stereochemically active in  $[Bi{OCH(CF_3)_2}_3thf]_2$  and occupies an octahedral site, a similar situation might be expected for the pentafluorophenoxide. However, in  $[Bi(OC_6F_5)_3(thf)_2]_2$  two thf ligands instead of one in  $[Bi{OCH(CF_3)_2}_3thf]_2$  are coordinated to the bismuth atom and the coordination geometry is best described as octahedral although with major distortion. Thus, it seems to be unlikely that in the dimeric bismuth alkoxides the lone pair occupies an ideal octahedral site. Formally, in  $[Bi(OC_6F_5)_3(toluene)]_2$  one toluene molecule displaces two thf molecules. The basic structure comprising a planar  $Bi_2(\mu-OAr)_2$  unit is retained and the O–Bi–O bond angles assigned to the OAr ligands do not significantly change compared with  $[Bi(OC_6F_5)_3(thf)_2]_2$ . Moreover these O–Bi–O bond angles are close to 90° in all three compounds and they all exhibit unsymmetrical alkoxide



Fig. 7. Molecular structure of  $[Bi(OC_6F_5)_3(thf)_2]_2$  [357]. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while O and F atoms are represented by different shades of grey from brighter to darker, respectively.

bridges. The Bi–O bond pattern within the dimeric  $Bi_2(\mu$ -OAr)\_2 unit is composed of one short primary Bi–O bond and a significantly longer secondary Bi–O bond. The bonding situation of the bismuth compounds might be explained by a bond pattern in which the primary Bi–O bonds are primarily of p-orbital character and the electrons of the spherical s-orbital do not contribute to the bonding scheme. The additional ligands (thf, arene,  $\mu$ -alkoxide) are bonded via the HOMO of the Lewis base which interacts with a  $\delta^*(Bi–O)$  orbital [9]. These secondary bonds are relatively weak and thus bismuth alkoxides were suggested to have a very low energy barrier between those molecular structures that have a noticeable vacant coordination site and those that do not [349]. The flat energy surface of these compounds is nicely demonstrated by the single crystal X-ray diffraction analyses of  $[Bi(OC_6F_5)_3(thf)_2]_2$  and its



Fig. 8. Molecular structure of  $[Bi(OC_6F_5)_3(toluene)]_2$  [357]. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while O and F atoms are represented by different shades of grey from brighter to darker, respectively.

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Table 3 Synthesis and characterization of homoleptic bismuth siloxides

Compound	Synthesis	Analyses	Literature
[Bi(OSiMe <sub>3</sub> ) <sub>3</sub> ]	A, C	<sup>1</sup> H, <sup>13</sup> C, <sup>29</sup> Si NMR, IR, XRD, DTA-TG	[352,383,384,394]
[Bi(OSiEt <sub>3</sub> ) <sub>3</sub> ]	С	<sup>1</sup> H, <sup>13</sup> C, <sup>29</sup> Si NMR, IR, DTA-TG	[384]
[Bi(OSi <i>i</i> Pr <sub>3</sub> ) <sub>3</sub> ]	С	<sup>1</sup> H, <sup>13</sup> C, <sup>29</sup> Si NMR, IR, XRD	[384]
[Bi(OSiPh <sub>3</sub> ) <sub>3</sub> (thf) <sub>3</sub> ]	В	<sup>1</sup> H, <sup>29</sup> Si NMR, IR, XRD	[364]
[Bi(OSiMe <sub>2</sub> <i>t</i> Bu) <sub>3</sub> ]	С	<sup>1</sup> H, <sup>13</sup> C, <sup>29</sup> Si NMR, IR, XRD, DTA-TG	[387]
$[Bi(OSiPh_2tBu)_3]$	C, D	<sup>1</sup> H, <sup>13</sup> C, <sup>29</sup> Si NMR, IR, XRD, DTA-TG	[358]
$[Bi{OSi(OtBu)_3}_3]$	A, C	<sup>1</sup> H, <sup>13</sup> C NMR, IR, TG	[386]
$[Bi\{OSi(OtBu)_2Ph\}_3]$	С	<sup>1</sup> H, <sup>13</sup> C NMR, IR	[386]

hexane solvate  $[Bi(OC_6F_5)_3(thf)_2]_2 \cdot C_6H_{14}$  [357]. Although the molecular structures of both compounds are close to each other, significant changes in bond lengths (Bi- $\mu$ -OC<sub>6</sub>F<sub>5</sub>: 2.245 and 2.661 Å versus 2.198 and 2.75 Å) and ArO–Bi–OAr bond angles (O–Bi–O: 83.2–98.2° versus 81.9–93.3°) were observed.

# 3.2. Bismuth siloxides

The first report on homoleptic bismuth siloxides dates back to 1968, when Schmidbaur and Bergfeld reported the synthesis of [Bi(OSiMe<sub>3</sub>)<sub>3</sub>] [383]. The compound was prepared via the metathesis route A. However, there have been some doubts about its purity and an unambiguous characterization was lacking until recently [384]. It was shown that the metathesis route is not well suited for the synthesis of [Bi(OSiMe<sub>3</sub>)<sub>3</sub>] mainly because the reaction of BiCl<sub>3</sub> and NaOSiMe<sub>3</sub> produces heterobimetallic bismuth oxo clusters faster than the metathesis reaction to give [Bi(OSiMe<sub>3</sub>)<sub>3</sub>] [352,385]. The high tendency to give heterobimetallic sodium bismuth oxo silanolates is explained by the similar ionic radii of Na<sup>+</sup> and Bi<sup>3+</sup> and was demonstrated by several single crystal structure analyses (see Section 3.3) [352,385]. The ease of M–O–M bond formation by elimination of  $R_3 SiOSiR_3$  (R = Me) is significantly reduced by more bulky triorganosilanolates. Noteworthy, the corresponding alkoxide [Bi(OtBu)<sub>3</sub>] is accessible via salt elimination in high yield [363,371]. The silanol-alcohol exchange C starting from  $[Bi(OtBu)_3]$  seems to be the most convenient synthetic protocol for bismuth siloxides and was used to prepare  $[Bi(OSiR_3)_3]$ (R = Me, Et, iPr) [384],  $[Bi{OSi(OtBu)_2R}_3]$  (R = OtBu, Ph)[386], [Bi(OSiMe<sub>2</sub>*t*Bu)<sub>3</sub>] [387] and [Bi(OSiPh<sub>2</sub>*t*Bu)<sub>3</sub>] [358] in high yields (Table 3). Alternatively, the amide-silanol exchange B might be employed as reported for [Bi(OSiPh<sub>3</sub>)<sub>3</sub>(thf)<sub>3</sub>] [364]. The reaction of triphenyl bismuth, which is a rare example of a commercially available organometallic compound, with silanols following route D is restricted to thermally stable bismuth siloxides as for instance [Bi(OSiPh<sub>2</sub>*t*Bu)<sub>3</sub>] [358] (Scheme 3).

In contrast to the simple bismuth alkoxides, the bismuth siloxides reported here are highly soluble in common organic solvents with an exception being  $[Bi(OSiPh_3)_3]$ . It should be mentioned that the bismuth siloxides are much more sensitive towards hydrolysis than  $[Bi(OtBu)_3]$ . This is remarkable, because they are accessible from  $[Bi(OtBu)_3]$  by its acid–base reaction with the corresponding triorganosilanol. Noteworthy, the latter is more acidic than the corresponding alcohol. This hydrolysis behaviour is explained by the tendency of silanols to

$BiCl_3$ + 3 NaOSiR <sub>3</sub>	- 3 NaCl	[Bi(OSiR <sub>3</sub> ) <sub>3</sub> ]	(A)
[Bi{N(SiMe <sub>3</sub> ) <sub>2</sub> } <sub>3</sub> ] + 3 HOSiR <sub>3</sub>	- 3 HN(SiMe <sub>3</sub> ) <sub>2</sub>	[Bi(OSiR <sub>3</sub> ) <sub>3</sub> ]	(B)
[Bi(OtBu) <sub>3</sub> ] + 3 HOSiR <sub>3</sub>	- 3 HOtBu	[Bi(OSiR <sub>3</sub> ) <sub>3</sub> ]	(C)
BiPh3 + 3 HOSiR3	- 3 C <sub>6</sub> H <sub>6</sub>	[Bi(OSiR <sub>3</sub> ) <sub>3</sub> ]	(D)

Scheme 3. Methods used for the synthesis of bismuth siloxides.

give water upon self-condensation. Thus, hydrolysis of bismuth siloxide first leads to triorganosilanols and Bi–OH groups. Both tend to self-condense whereby water is produced. Thus, hydrolysis proceeds until a bismuth oxo cluster is formed, which is either relatively stable towards hydrolysis or insoluble. As a result several polynuclear bismuth oxo silanolates have been prepared (see Section 3.3).

In 2005 a single crystal structure analysis of  $[Bi(OSiMe_3)_3]$  was reported, which reveals an unexpected trimeric structure as a result of weak intermolecular bismuth–oxygen interactions (Fig. 9) [384]. Primary Bi–O bonds in the range 2.041(3)–2.100(3) Å and secondary Bi–O bonds in the range 2.686(3)–3.230(3) Å were observed. In contrast to



Fig. 9. Molecular structure of trimeric [Bi(OSiMe<sub>3</sub>)<sub>3</sub>] [384]. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while O and Si atoms are represented by different shades of grey from brighter to darker, respectively.



Fig. 10. Molecular structure of  $[Bi(OSiMe_2tBu)_3]$  [387]. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while O and Si atoms are represented by different shades of grey from brighter to darker, respectively.

 $[Bi(OSiMe_3)_3]$  the more sterically hindered bismuth siloxides  $[Bi(OSiiPr_3)_3]$  [384] and  $[Bi(OSiMe_2tBu)_3]$  [387] are monomeric in the solid state (Fig. 10).

The bismuth siloxides show marked differences in their thermal behaviour. [Bi(OSiMe<sub>2</sub>tBu)<sub>3</sub>] was evaporated in vacuo  $(10^{-2} \text{ Torr})$  without significant decomposition in the temperature range 150–160 °C. Under similar conditions  $[Bi(OSiiPr_3)_3]$ is only partially evaporated and shows some decomposition. The trimethylsilanolate derivative [Bi(OSiMe<sub>3</sub>)<sub>3</sub>] is not volatile and decomposes at temperatures below 100 °C. In the case of  $[Bi{OSi(OtBu)_3}_3]$  decomposition at a temperature of approximately 90 °C was observed and the final hybrid material is expected to be composed of Bi<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. A similar thermal behaviour was demonstrated for a large variety of metal siloxides containing the  $OSi(OtBu)_3$  substituent [388–393]. In contrast, one might expect that the thermally induced decomposition of bismuth silanolates of the type  $[Bi(OSiR_3)_3]$  (R = alkyl) and especially of [Bi(OSiMe<sub>3</sub>)<sub>3</sub>] should give the pure bismuth oxide upon elimination of the corresponding hexaorganodisiloxane R<sub>3</sub>SiOSiR<sub>3</sub>. However, for these compounds bismuth silicates are also formed, although with a significantly lower silicon content. Most interestingly, decomposition of [Bi(OSiMe<sub>2</sub>*t*Bu)<sub>3</sub>] [387] cleanly produces crystalline Bi<sub>12</sub>SiO<sub>20</sub>. The latter belongs to the large family of sillenite type compounds [35-38]. This class of compounds was extensively studied as a result of interesting optical properties such as photorefractivity, photoconductivity, piezoelectricity and optical activity [34,39-42]. For example, neodymium-doped Bi12SiO20 was reported to show luminescence properties which make it a promising material with respect to laser action [234–236].

[Bi(OSiPh<sub>2</sub>*t*Bu)<sub>3</sub>] shows an increased thermal stability as compared with the bismuth tris(trialkylsiloxides). Thus thermal decomposition is observed above a temperature of 250 °C and partially results in the formation of elemental bismuth. The most striking feature of [Bi(OSiPh<sub>2</sub>*t*Bu)<sub>3</sub>] is the formation of a dimer as a result of weak bismuth  $\pi$ -arene coordination (Fig. 11) [358]. As was stated in Section 3.1 this weak Lewis acid–Lewis base



Fig. 11. Molecular structure of [Bi(OSiPh<sub>2</sub>*t*Bu)<sub>3</sub>] [358]. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while O and Si atoms are represented by different shades of grey from brighter to darker, respectively.

interaction might be described by a bond pattern in which the HOMO of the Lewis base interacts with the  $\delta^*(Bi-O)$  orbital. This type of bismuth  $\pi$ -arene interaction is typical for bismuth compounds bearing electron-withdrawing substituents. The distance between the bismuth atom in  $[Bi(OSiPh_2tBu)_3]_2$  and the ring-centroid of the coordinated arene amounts to 3.34 Å, which is in the upper range of Bi $-\pi$ -arene centroid distances reported previously [374–378]. These are typically found in the range 2.7–3.7 Å.

# 3.3. Bismuth oxo clusters

Hydrolysis of metal alkoxides  $[M(OR)_z]_n$  and metal siloxides  $[M(OSiR_3)_z]_n$  proceeds by the formation of small aggregates of metal-oxo(hydroxo) clusters, which are further linked by hydrolysis-condensation reactions to give compounds of the general type  $[MO_x(OH)_y(OR)_{z-y-2x}]_n$  (R = alkyl, trialkylsilyl). The latter are converted to the parent metal oxides or silicates by additional steps such as calcination and sintering. A thorough understanding of the hydrolysis process might provide information on the problem how to control the composition and morphology of bismuth-containing (nano)materials produced by way of wet chemical processes. Therefore it is of great interest to identify metal oxo clusters of different sizes, which are formed upon partial hydrolysis of the same starting material. A comparison of their molecular structures with the solid state structures of the corresponding metal oxides or hydroxides might lead to a better understanding of the stepwise growth process of metal oxides. Metal oxo alkoxides and siloxides serve as model compounds even for the aqueous solution behaviour of metal oxo hydroxides. The alkoxide and siloxide ligands shield the metal oxo core, and by a variation of their steric demand the size of the metal oxo cluster core is controlled. Tables 4 and 5 list those bismuth oxo alkoxides and siloxides that have been structurally characterized by single crystal X-ray diffraction analyses.

It is well accepted that the aqueous chemistry of bismuth is dominated by hexanuclear cations of the type

Table 4 Structurally characterized homoleptic bismuth oxo alkoxides and oxo aryloxides

Compound	Analysis	Literature
$\overline{[\text{Bi}_4\text{O}_2(\text{O}t\text{Bu})_8]}$	XRD	[365]
$[Bi_6O_3(OC_6F_5)_{12}]$	XRD, <sup>19</sup> F NMR	[349]
$[Bi_8O_4(OC_6F_5)_{16}]$	XRD, <sup>19</sup> F NMR	[349]
$[Bi_9O_8(OEt)_6](ClO_4)_5$	XRD, <sup>1</sup> H, <sup>13</sup> C NMR, IR	[407]
$[Bi_9O_7(OC_6F_5)_{13}]$	XRD, <sup>19</sup> F NMR	[349,413]
$[Bi_9O_7(OC_6H_3Cl_2-2,6)_{13}]$	XRD, <sup>1</sup> H NMR	[355]
$[Bi_8O_4(p-tBucalix[8]aren)]$	XRD	[410]
[BiOOMe]	XRD	[368]

Table 5

Structurally characterized homoleptic bismuth oxo siloxides

Compound	Analysis	Literature
[Bi <sub>4</sub> O <sub>2</sub> (OSiEt <sub>3</sub> ) <sub>8</sub> ]	XRD, IR, <sup>1</sup> H NMR	[385]
$[Bi_9O_7(OSiMe_3)_{13}]$	XRD, IR	[385]
[Bi <sub>18</sub> O <sub>18</sub> (OSiMe <sub>3</sub> ) <sub>18</sub> ]	XRD, IR	[385]
$[Bi_{20}O_{18}(OSiMe_3)_{24}]$	XRD, IR	[385]
$[\mathrm{Bi}_{22}\mathrm{O}_{26}(\mathrm{OSiMe}_2 t\mathrm{Bu})_{14}]$	XRD, IR, DTA-TG	[385,387]

 $[Bi_6O_{4+x}(OH)_{4-x}]^{(6-x)+}$  [395], which are the major species at low concentration (0.1 M) at pH < 3. The hexanuclear  $[Bi_6O_8]^{2+}$ motif as found in  $[Bi_6O_{4+x}(OH)_{4-x}]^{(6-x)+}$  is refered to as motif A (Fig. 12). The latter was observed as central structural unit in a large variety of compounds such as bismuth oxo hydroxo nitrates [396–400], bismuth oxo hydroxo perchlorates [401–403], bismuth oxo trifluoroacetate [404] and bismuth oxo citrate [405,406].

It was suggested earlier that in aqueous solution the hexanuclear clusters transform into nonanuclear species with increasing pH, but direct evidence was lacking [395]. It was only very recently that the first nonanuclear bismuth oxo hydroxo cation was isolated from aqueous solution, namely  $[Bi_9(\mu_3-O)_8(\mu_3-OH)_6]^{5+}$  [407]. The latter is easily transformed into the isostructural alkoxide  $[Bi_9(\mu_3-O)_8(\mu_3-OEt)_6]^{5+}$  by reaction with ethanol. This is a nice example that demonstrates the strong structural relationship between bismuth oxo hydroxides and the





Fig. 13. View of the tetranuclear  $[Bi_4O_6]$  motif B in  $[Bi_9(\mu_3-O)_8(\mu_3-OEt)_6]^{5+}$  [407]. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while grey spheres represent O atoms.

corresponding alkoxides. The basic building unit is described as a  $[Bi_4(\mu_3-O)_2(\mu_3-OR)_4]$  (R=H, Et) subunit that contains the basic structural  $[Bi_4X_6]$  (X = O) motif, hereafter referred to as motif B (Fig. 13). This structural fragment constitutes one main structural subunit found in bismuth oxo chemistry as was noted earlier by Whitmire et al. [349]. The molecular structure of  $[Bi_9(\mu_3-O)_8(\mu_3-OEt)_6]^{5+}$  is shown in Fig. 14.

Motif B is identified in several other bismuth oxo species such as  $[Bi_4O_2(OtBu)_8]$  [365],  $[Bi_4O_2(OSiEt_3)_8]$  [384], the complex anion  $[Bi_2O_2(OH)_6]^{4-}$  in Na<sub>6</sub> $[Bi_2O_2(OH)_6](OH)_2 \cdot 2H_2O$ [408],  $[Bi_4O_2(OOCCF_3)_8]$  [409],  $[Bi_8O_4(p-tBucalix[8]arene)]$ [410] as well as in more complex homo- and heterometallic bismuth oxo structures [349,352,385]. The above-mentioned compounds might be assigned the general formulae  $[BiOX]_2 \cdot 2BiX_3$ (X = OR, OSiR<sub>3</sub>, OOCR) and  $[BiOX]_2 \cdot 4X$  (X = OH<sup>-</sup>), respectively. The smallest fragment [BiOX] is realised in the oxo alkoxide [BiOOMe] [368], in the hydroxy nitrate  $[Bi_2O_2(OH)(NO_3)]$ [411], as well as in [BiOCI], which is the hydrolysis product



Fig. 14. Molecular structure of  $[Bi_9(\mu_3-O)_8(\mu_3-OEt)_6]^{5+}$  [407]. The polyhedron represents the pentanuclear subunit  $[Bi_5O_8]^-$  (motif D). The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while grey spheres represent O atoms.



Fig. 15. Graphical representation of basic building units, which are typically found in bismuth oxo clusters.

observed upon addition of water to bismuth trichloride. The central structural motif in these compounds is best described as an Aurivillius-type  $[Bi_2O_2]^{2+}$  layer, that is produced from the [Bi<sub>4</sub>O<sub>2</sub>X<sub>4</sub>] subunit of type B by removal of two Bi atoms and four X atoms. The trend to give compounds of the general formula [BiOX]<sub>2</sub>·2BiX<sub>3</sub> with B-type structure exemplifies that hydrolysis of bismuth compounds is easily followed by condensation to give Bi-O-Bi bonding. It is somewhat surprising that discrete trinuclear fragments of type C with the general formula  $[Bi_3(\mu_3-O)X_3]$ , which is produced from the type B structure by removal of one bismuth atom and two groups X, have not been reported. Motif A as well as motif B both contain the structural fragment of type C with a µ<sub>3</sub>-oxo ligand (Fig. 15), but  $[Bi_3(\mu_3-OH)(OOCCF_3)_8]$  is the only fully characterized example of a discrete molecule that is composed of a trinuclear unit capped by a µ<sub>3</sub>-coordinating oxo or hydroxo ligand [404,409]. The latter carboxylate might also be formulated as [Bi(OH)(OOCCF<sub>3</sub>)<sub>2</sub>]·2[Bi(OOCCF<sub>3</sub>)<sub>3</sub>] and constitutes the primary hydrolysis product of bismuth trifluoroacetate.

The tetranuclear  $[Bi_4(\mu_3-O)_2(\mu_3-OR)_4]$  building block of type B can also be built from the hexanuclear  $[Bi_6O_{4+x}(OH)_{4-x}]^{(6-x)+}$  core structure A by removal of two bismuth atoms and the attached oxygen atoms from the latter. Removal of only one bismuth atom leads to the pentanuclear  $[Bi_5O_8]^-$  motif D (Fig. 16), which is part of the molecular structures of  $[Bi_{15}Na_3O_{18}(OSiMe_3)_{12}]$  [352],  $[Bi_8O_6(O_2CNiPr_2)_{12}]$ [412] as well as of  $[Bi_9(\mu_3-O)_8(\mu_3-OR)_6]^{5+}$  (R = H, Et) [407].



Fig. 16. View of the pentanuclear  $[Bi_5O_8]^-$  motif D. The black spheres correspond to Bi atoms and the grey spheres to O atoms.



Fig. 17. Molecular structure of  $[Bi_9O_7(OSiMe_3)_{13}]$  [385]. The grey polyedron represents the hexanuclear subunit A. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while O and Si atoms are represented by different shades of grey from brighter to darker, respectively.

In  $[Bi_{15}Na_3O_{18}(OSiMe_3)_{12}]$  three pentagonal pyramidal bismuth oxo units of type D are connected via coordination to three central sodium atoms; in  $[Bi_8O_6(O_2CNiPr_2)_{12}]$  two pentagonal Bi-pyramids are edge-sharing to give an octanuclear subunit; in  $[Bi_9(\mu_3-O)_8(\mu_3-OR)_6]^{5+}$  (R = H, Et) three pentagonal pyramids are edge-sharing to give a nonanuclear bismuth oxo cluster (Fig. 14). In addition to  $[Bi_9(\mu_3-O)_8(\mu_3-OEt)_6]^{5+}$  two nonanuclear bismuth oxo aryloxides, namely  $[Bi_9O_7(OC_6F_5)_{13}]$ [349,413] and  $[Bi_9O_7(OC_6H_3Cl_2-2,6)_{13}]$  [355], and a nonanuclear bismuth oxo siloxide, namely  $[Bi_9O_7(OSiMe_3)_{13}]$  [385], have been reported. In contrast to  $[Bi_9(\mu_3-O)_8(\mu_3-OR)_6]^{5+}$  these compounds are composed of a hexanuclear unit of type A to which three bismuth alkoxide/siloxide units are coordinated (Fig. 17).

We have recently reported several polynuclear bismuth oxo clusters which might be described in terms of assemblies of the hexanuclear motif A [385,387]. In addition to the molecular structure of [Bi<sub>9</sub>O<sub>7</sub>(OSiMe<sub>3</sub>)<sub>13</sub>] those of the homometallic siloxides [Bi<sub>18</sub>O<sub>18</sub>(OSiMe<sub>3</sub>)<sub>18</sub>], [Bi<sub>20</sub>O<sub>18</sub>-(OSiMe<sub>3</sub>)<sub>24</sub>] and [Bi<sub>22</sub>O<sub>26</sub>(OSiMe<sub>2</sub>*t*Bu)<sub>14</sub>] as well as those of the heterometallic clusters [Bi33NaO38(OSiMe3)24] and [Bi50-Na<sub>2</sub>O<sub>64</sub>(OH)<sub>2</sub>(OSiMe<sub>3</sub>)<sub>22</sub>] were examined. The assembly of the  $[Bi_6O_8]^{2+}$  motif A through Bi-Bi edges results in the final bismuth oxo clusters with partial substitution of bismuth sites by sodium atoms in case of the heterometallic compounds. In  $[Bi_{18}O_{18}(OSiMe_3)_{18}]$  and  $[Bi_{20}O_{18}(OSiMe_3)_{24}]$ four type A fragments are assembled, in [Bi22O26(OSiMe2t-Bu)<sub>14</sub>] 6, in [Bi<sub>33</sub>NaO<sub>38</sub>(OSiMe<sub>3</sub>)<sub>24</sub>] 10 and in [Bi<sub>50</sub>Na<sub>2</sub>O<sub>64</sub>-(OH)<sub>2</sub>(OSiMe<sub>3</sub>)<sub>22</sub>] 20. In Figs. 18-20 the molecular structures of  $[Bi_{18}O_{18}(OSiMe_3)_{18}]$ ,  $[Bi_{22}O_{26}(OSiMe_2tBu)_{14}]$  and [Bi<sub>50</sub>Na<sub>2</sub>O<sub>64</sub>(OH)<sub>2</sub>(OSiMe<sub>3</sub>)<sub>22</sub>], respectively, are shown. The



Fig. 18. Molecular structure of  $[Bi_{18}O_{18}(OSiMe_3)_{18}]$  [385]. The grey polyhedra represent the four hexanuclear subunits A. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while O and Si atoms are represented by different shades of grey from brighter to darker, respectively.

hexanuclear  $[Bi_6O_8]^{2+}$  motifs of type A are highlighted in grey in the homometallic compounds shown in Figs. 18 and 19.

The above mentioned bismuth oxo clusters are composed of different numbers of edge-sharing  $[Bi_6O_8]^{2+}$  motifs A. The correlation of this number with the bismuth oxo cluster size is demonstrated in Fig. 21. Extension of the number of type A units to infinite results in a nearly f.c.c. packing of bismuth atoms, which is also realised in bismuth compounds such as tetragonal  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> and cubic  $\delta$ -Bi<sub>2</sub>O<sub>3</sub>. Both solid state structures can be produced from the CaF<sub>2</sub>-type structure by assuming a defect oxygen sublattice.



Fig. 20. Molecular structure of  $[Bi_{50}Na_2O_{64}(OH)_2(OSiMe_3)_{22}]$  [385]. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while O and Si atoms are represented by different shades of grey from brighter to darker, respectively. Grey spheres represent the sodium atoms.

In the solid state structures of both  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> and  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> the oxygen atoms are tetracoordinated and occupy 3/4 of the tetrahedral voids in the f.c.c. packing of the bismuth atoms. In contrast to  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> the oxygen atoms in  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> are statistically distributed, which is characteristic for the high oxide ion conductivity of  $\delta$ -Bi<sub>2</sub>O<sub>3</sub>. Comparing the solid state structures of  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> and  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> with those of the molecular clusters, a significant difference is observed. In the bismuth oxo clusters the tetrahedral voids are filled with oxygen atoms whereas in  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> and  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> only 3/4 of these voids are occupied with oxygen atoms. Thus, the polynuclear bismuth oxo clusters might be regarded as a "cut-out" of the solid state structure of  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> or  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> with an excess of oxygen in the respective sublattice. Noteworthy, in the sodium-containing compounds even some octahedral voids are occupied by oxygen atoms. Such "defects" might also occur in solid state structures of heterometallic bismuth compounds, especially in those that have been prepared starting from sodium metalates. It is to be expected that the elec-



Fig. 19. Molecular structure of  $[Bi_{22}O_{26}(OSiMe_2tBu)_{14}]$  [385,387]. The grey polyhedra represent the six hexanuclear subunits A. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, while O and Si atoms are represented by different shades of grey from brighter to darker, respectively.

Fig. 21. Correlation between the number of edge-sharing  $[Bi_6O_8]^{2+}$  motifs A and the size of the bismuth oxo siloxide cluster [385]. Partial substitution of bismuth atoms with sodium atoms is observed in the heterometallic compounds.

tronic properties of such "defect" compounds might be different from those of the pure material. For example, it was reported that the photocatalytic activity of monoclinic  $BiVO_4$  prepared from sodium vanadate and bismuth nitrate is changed when using a wet chemical route instead of a solid state reaction [160,161]. We assume that the difference in photocatalytic activity might be simply the result of a different degree of substitution of bismuth by sodium atoms. However, this hypothesis has yet to be verified.

The coordination chemistry of bismuth within the molecular bismuth oxo clusters is characterized by strong distortions from ideal bismuth oxygen polyhedra caused by the presence of the lone pair at the bismuth atom. Predominantly, distorted pseudotetrahedra, pseudo-trigonal bipyramids and pseudo-octahedra are observed with primary bismuth-oxygen bond lengths typically in the range 2.0–2.5 Å. For most of the bismuth atoms additional secondary Bi-O bonds complete the coordination sphere that are significantly shorter than the sum of the van der Waals radii of oxygen and bismuth ( $r_{vdW}(O)$  1.50 Å [414],  $r_{\rm vdW}$ (Bi) 2.40 Å) [9]. In  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> the bismuth atom shows a *pseudo*-trigonal bipyramidal coordination  $BiO_4X$  (X = lone pair) with Bi-O bond distances of 2.096(4), 2.128(7), 2.253(7) and 2.463(7) Å [77]. This bonding situation comes closest to the majority of bismuth atoms which are located within the central metal oxo core of the homometallic bismuth oxo clusters.

In addition to studies on molecular bismuth oxo clusters in solution, the gas phase chemistry of bismuth oxo cluster cations and anions was reported [415–418]. Mass spectrometry was used to analyse the bismuth oxo cluster distribution and to study the interaction of the latter cations with alkenes. Magic numbers for the oxo cluster formation were found. In the anionic series predominantly clusters of the type  $(Bi_2O_3)_n BiO_2^-$ ,  $(Bi_2O_3)_n O^$ and  $(Bi_2O_3)_nO_2^-$  are formed, whereas in the cationic series clusters of the type  $(Bi_2O_3)_nBiO^+$ ,  $(Bi_2O_3)_n^+$  and  $(Bi_2O_3)_nO^+$ dominate. A theoretical study on the structural and electronic properties of bismuth oxo cluster cations of the type  $[Bi_3O_v]^+$ (y=3-6) and  $[Bi_4O_y]^+$  (y=6-8) and their reactivity with ethene in the presence of oxygen was also reported [419]. For the Bi<sub>3</sub>O<sub>4</sub><sup>+</sup> cluster a six-membered bismuth oxygen ring that is capped by a µ3-oxo ligand had been suggested as the most stable structure. This arrangement is similar to the basic molecular structure of the trimer [Bi(OSiMe<sub>3</sub>)<sub>3</sub>]<sub>3</sub>, that consists of a sixmembered bismuth oxygen ring that is capped by  $\mu_3$ -siloxide ligands from both faces [384]. The structure of  $Bi_4O_6^+$  was suggested to closely resemble the molecular structure of  $P_4O_6$ . It was shown that the former cluster might serve as a model compound for the oxidation process of alkenes. Noteworthy, the presence of molecular oxygen that reacts with Bi<sub>4</sub>O<sub>6</sub><sup>+</sup> prior to the oxidation of ethene is vital for the alkene oxidation process.

## 4. Heterometallic precursors and model compounds

#### 4.1. Bismuth/alkali metal oxo clusters

In the last decade much effort has been devoted to the development of improved strategies for the synthesis of binary and multimetallic metal oxides with special focus on thin films and nanoparticles [1-6]. The main reason is that these materials are difficult to prepare using traditional techniques. It is now widely accepted that size, morphology and physical properties of materials prepared via soft chemical routes such as the sol-gel process, chemical bath deposition, co-precipitation, metal organic decomposition or MOCVD might differ from those of the same material prepared via conventional solid state reaction. One example taken from the heterometallic bismuth oxide family is the bismuth vanadate BiVO<sub>4</sub> that was reported to show different properties such as variable photocatalytic activity depending on the synthetic strategy used for its preparation [160,161,165,168]. However, as outlined in Section 3.3 the results should be considered with care, since partial substitution of bismuth by sodium might also alter the physical properties of the final material. Therefore, not only the morphology but also the exact elemental composition of the final material has to be carefully investigated. In case of the use of sodium as part of the starting material special attention should be paid to the incorporation of the alkali metal within the molecular precursors and thus also within the final bismuth oxide-based materials. Bismuth and sodium both show a variable metal oxygen coordination chemistry and as a result of their similar ionic radii the replacement of bismuth atoms in the bismuth oxide framework is easily achieved  $[r(Bi^{3+})=117 \text{ pm}; r(Na^+)=116 \text{ pm};$ coordination number CN = 6 [420,421]. This is nicely demonstrated by a number of bismuth-sodium alkoxides and siloxides that have been structurally characterized (Table 6). In contrast to 13 examples with sodium only one example of a heterobimetallic compound containing the smaller lithium cation, namely  $[Bi_3Li_5O_2(OSiMe_3)_2(OtBu)_8]$  [354], and two examples containing the larger potassium cation, namely [BiK(OtBu)<sub>4</sub>] [351] and [Bi<sub>15</sub>KO<sub>15</sub>(OSiMe<sub>3</sub>)<sub>16</sub>(HOSiMe<sub>3</sub>)] [422], have been characterized by single crystal X-ray diffraction analysis.

Table 6

Heterometallic bismuth metal alkoxides and silanolates containing main group metals

Compound	Literature	
Bi–Li–O		
$[Bi_3Li_5O_2(OSiMe_3)_2(OtBu)_8]$	[354]	
Bi–Na–O		
$[Bi_2Na_4O(OtBu)_8]$	[351]	
$[Bi_3NaO(OC_6F_5)_8(thf)]$	[424]	
$[Bi_4NaO_2(OC_6F_5)_9(thf)_2]$	[349]	
$[Bi_4Na_2O_2(OC_6F_5)_{10}(thf)_2]$	[349]	
$[BiNa(OC_6F_5)_4(thf)]$	[353]	
$[Bi_2Na_4O(OC_6F_5)_8(thf)_4]$	[353]	
[Bi <sub>2</sub> Na <sub>4</sub> O(OSiMe <sub>3</sub> ) <sub>8</sub> ]	[352]	
[Bi <sub>10</sub> Na <sub>5</sub> O <sub>7</sub> (OH) <sub>6</sub> (OSiMe <sub>3</sub> ) <sub>15</sub> ]	[352]	
[Bi <sub>14</sub> Na <sub>8</sub> O <sub>18</sub> (OSiMe <sub>3</sub> ) <sub>14</sub> (thf) <sub>4</sub> ]	[352]	
[Bi <sub>15</sub> Na <sub>3</sub> O <sub>18</sub> (OSiMe <sub>3</sub> ) <sub>12</sub> ]	[352]	
[Bi <sub>18</sub> Na <sub>4</sub> O <sub>20</sub> (OSiMe <sub>3</sub> ) <sub>18</sub> ]	[385]	
[Bi <sub>33</sub> NaO <sub>38</sub> (OSiMe <sub>3</sub> ) <sub>24</sub> ]	[385]	
[Bi50Na2O64(OH)2(OSiMe3)22]	[385]	
Bi-K-O		
$[BiK(OtBu)_4]$	[351]	
$[Bi_{15}KO_{15}(OSiMe_3)_{16}(HOSiMe_3)]$	[422]	
Bi–Ba–O		
$[Bi_4Ba_4O_2(OEt)_{12}(thd)_4]$	[425]	



Fig. 22. Molecular structure of [Bi<sub>2</sub>Na<sub>4</sub>O(OSiMe<sub>3</sub>)<sub>8</sub>] [352]. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, the large grey spheres correspond to Na atoms and the O and Si atoms are represented by different shades of grey from brighter to darker, respectively.

Among the sodium-containing examples the most prominent structural motif is the hexanuclear metal oxo cluster of the type  $[Bi_2Na_4O(OR)_8]$  (R = OtBu, OSiMe\_3, OC\_6F\_5) [351–353], which is structurally related to the  $[Bi_6O_8]^{2+}$  cation of type A. In  $[Bi_2Na_4O(OR)_8]$  a  $[Bi_6O_9]$ -motif is found, which can be built from  $[Bi_6O_8]^{2+}$  by placing one additional oxygen atom on the center of the  $\{Bi_6\}$ -octahedron. Noteworthy, the isostructural heterobimetallic antimony oxo alkoxides, namely  $[Sb_2Na_4O(OSiMe_3)_8]$  [423] and  $[Sb_2M_4O(OSiMe_3)_8(thf)_n]$  (M = Na, n = 0; M = K, n = 0, 4) [351] have also been reported. In Fig. 22 the molecular structure of  $[Bi_2Na_4O(OSiMe_3)_8]$  is shown.

All compounds of the type  $[Bi_2Na_4O(OR)_8]$  show a dynamic behaviour in solution that involves a fast exchange process of the OR ligands. It was shown by means of solid state NMR, variable-temperature NMR in solution, crystallography and a theoretical study that the group 15 atoms both in the solid state and in solution are located cis to each other in the octahedron. The single crystal X-ray diffraction studies of the thf-free compounds reveal that both the group 15 atoms and the alkali metals occupy each metal atom position with occupancies of 1/3 and 2/3, respectively. Thus, the ideal  $\mu_6$ -coordination of the central oxygen atom is most likely in all cases a result of disorder rather than the result of a similar Lewis-acidity of bismuth and sodium.

The polynuclear bismuth oxo cluster  $[Bi_{15}Na_3O_{18}-(OSiMe_3)_{12}]$  incorporates three sodium cations and might be described as composed of three  $[Bi_5O_{12}]^{9-}$  units that are connected via oxygen atoms to the central sodium atoms (Fig. 23). The  $[Bi_5O_{12}]^{9-}$  units are composed of five bismuth atoms that occupy the corners of a square pyramid. This subunit is also found in other bismuth-oxo clusters such as  $[Bi_9(\mu_3-O)_8(\mu_3-OR)_6]^{5+}$  (R = H, Et) [407], and can be reduced



Fig. 23. Molecular structure of  $[Bi_{15}Na_3O_{18}(OSiMe_3)_{12}]$  [352]. The large black spheres correspond to Bi atoms and the smaller ones to C atoms, the large grey spheres correspond to Na atoms and the O and Si atoms are represented by different shades of grey from brighter to darker, respectively.

to the pentanuclear  $[Bi_5O_8]^-$  motif D by removal of four O atoms. For a more detailed discussion of the type D structures see Section 3.3.

A seminal example with regard to partial substitution of bismuth atoms by sodium atoms is the high-nuclearity cluster  $[Bi_{33}NaO_{38}(OSiMe_3)_{24}]$  (Fig. 24). Its molecular structure is closely related to the pure polynuclear bismuth oxo clusters but also shows the incorporation of oxygen atoms within hexanuclear units as was observed for  $[Bi_2Na_4O(OR)_8]$ . The cluster contains 33 bismuth atoms but only one sodium atom. Additionally, the sodium atom and one bismuth atom are disordered and occupy the same position with an occupancy of 50% each. This demonstrates that bismuth is easily replaced by sodium, if a charge balance is required. A second example is provided by  $[Bi_{50}Na_2O_{64}(OH)_2(OSiMe_3)_{22}]$  (Fig. 20).

#### 4.2. Bismuth/transition metal complexes

The formation of thin films of heterometallic oxides with well-defined properties is of utmost importance for the microelectronics industry. The most convenient synthetic methods for thin film formation are the sol–gel process and metal organic vapour deposition (MOCVD). Synthetic protocols for both of these techniques usually make use of two metal-containing precursor that are mixed prior to reaction to give the mixed metal oxide. These two precursors often have different physical properties, hydrolytic stability and decomposition characteristics. The resulting precursor mismatch might result in poor film uniformity, low efficiency of deposition or poor control over the composition of the final material. A potential solution to this problem is use of the so-called single-source precursor approach. Different techniques such as the sol–gel process, MOCVD and



Fig. 24. Molecular structure of [Bi<sub>33</sub>NaO<sub>38</sub>(OSiMe<sub>3</sub>)<sub>24</sub>] [385]. The two central metal atom positions, highlighted in medium grey, represent bismuth and sodium atoms with an occupancy of 50% each. The large black spheres correspond to Bi atoms and the smaller ones to C atoms and the O and Si atoms are represented by different shades of grey from brighter to darker, respectively.

atomic layer deposition (ALD) offer the disposition of single source precursors. An ideal single source precursor contains the required elements with the appropriate ratio in a single molecule that upon decomposition or hydrolysis-condensation allows for the formation of well-defined bimetallic or multimetallic oxides under mild reaction conditions. It was shown by numerous examples that the crystalline material is formed at significantly lower temperature as compared with solid state reaction. This is attributed to the intimate mixing of the elements in a single molecule, which diminishes diffusion problems in the following reaction steps. Motivated by the high potential of this synthetic approach several research groups started to seek for bismuth-containing single source precursors for advanced materials (Table 7). A recent review by Whitmire and coworkers provides a comprehensive overview on their work entitled "Heterobimetallic bismuth-transition metal coordination complexes as single-source molecular precursor for the formation of advanced oxide materials" [426]. For early transition metals their work is focused on bifunctional ligands derived from salicylic acid (H<sub>2</sub>sal). One instructive example is  $[Bi_2Nb_2O(OEt)_2(sal)_4(Hsal)_4]$  the molecular structure of which is shown in Fig. 25 [248].

The complex contains the metal atoms in a 1:1 molar ratio together with a large amount of oxygen atoms. The compound decomposes on heating in air for 2 h at 750 °C to produce mainly the metastable high temperature phase of BiNbO<sub>4</sub> that crystallises in a triclinic setting. The orthorhombic low-temperature form of BiNbO<sub>4</sub> is found as a minor product. If the reaction time for the sintering process is prolonged or the temperature is increased conversion of the metastable phase into the lowtemperature phase is observed. In addition disproportionation of the bismuth niobate BiNbO<sub>4</sub> into Nb<sub>2</sub>O<sub>5</sub> and Bi<sub>5</sub>Nb<sub>3</sub>O<sub>15</sub> takes place at higher temperatures. The results presented by Thurston and Whitmire nicely demonstrate that the initial formation of BiNbO<sub>4</sub> is kinetically controlled. However, a study on the thermal decomposition of a similar bimetallic complex, namely  $[Bi_2Ti_4(OiPr)(sal)_{10}(Hsal)(H_2O)]$ , shows that the outcome of the decomposition process is not easily predictable. The molecular structure of the heterometallic complex is depicted in Fig. 26 [99].



Fig. 25. Graphical representation of the molecular structure of [Bi<sub>2</sub>Nb<sub>2</sub>O-(OEt)<sub>2</sub>(sal)<sub>4</sub>(Hsal)<sub>4</sub>] in the solid state [248].

Table 7

Selected examples of heterometallic bismuth compounds with oxygen-containing ligands and their thermolysis products

Compound	Thermolysis product	Literature
$\begin{array}{c} Bi-Ti-O\\ [BiTi_2O(iOPr)_9]\\ [BiTi_2O(OEt)_9]\\ [Bi_4Ti_3O_4(OEt)_{16}]\\ [Bi_2Ti_3(sal)_8(Hsal)_2]\\ [Bi_2Ti_4(OiPr)(sal)_{10}(Hsal)]\\ [BiTi_4(OiPr)_7(sal)_6]\\ [Bi_4Ti_4(OiPr)_8(sal)_{10}]\\ [Bi_8Ti_8(OiPr)_{16}(sal)_{20}] \end{array}$	$\begin{array}{l} Bi_{2}Ti_{2}O_{7}{}^{a,b}, Bi_{2}Ti_{4}O_{11}{}^{a,c}\\ Bi_{4}Ti_{3}O_{12}{}^{d}, Bi_{2}Ti_{4}O_{11} \ (1000\ ^{\circ}C)\\ Bi_{4}Ti_{3}O_{12}\\ Bi_{4}Ti_{3}O_{12}{}^{d}, Bi_{2}Ti_{4}O_{11}\\ Bi_{4}Ti_{3}O_{12}{}^{d}, Bi_{2}Ti_{4}O_{11}\\ \end{array}$	[100] [100] [99] [99] [114] [114] [114]
$ \begin{array}{l} \text{Bi-M-O} (M = \text{Nb}, \text{Ta}) \\ [\text{Bi}_2\text{M}_2\text{O}(\text{OEt})_2(\text{sal})_4(\text{Hsal})_4], [\text{Bi}\text{M}_4\text{O}_4(\text{O}i\text{Pr})_4(\text{sal})_4(\text{Hsal})_3] \\ [\text{Bi}_2\text{M}_2(\text{OR})_4(\text{sal})_4(\text{Hsal})_4] (\text{R} = \text{Et}, i\text{Pr}) \end{array} $	BiNbO <sub>4</sub> (650 $^{\circ}$ C) or Bi <sub>5</sub> Nb <sub>3</sub> O <sub>15</sub> , Nb <sub>2</sub> O <sub>5</sub> (850 $^{\circ}$ C) BiNbO <sub>4</sub> <sup>d</sup> , Bi <sub>5</sub> Nb <sub>3</sub> O <sub>15</sub> , Bi <sub>2</sub> O <sub>3</sub>	[248] [99]
$\begin{split} &\text{Bi-Mo-O} \\ & [\text{Cp}_2\text{Mo}(\text{OEt})_2\text{Bi}(\text{OEt})_2\text{Cl}] \\ & [\{(\text{CH}_3)\text{C}_3\text{H}_4\}\text{Mo}(\text{CO})_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2\text{Bi}\text{Cl}_2] \\ & [\{(\text{CH}_3)\text{C}_3\text{H}_4\}\text{Mo}(\text{CO})_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3\text{Bi}(\text{thf})][\text{BF}_4] \\ & [\{(\text{CH}_3)\text{C}_3\text{H}_4\}\text{Mo}(\text{CO})_2\text{Bi}(\text{OEt})_4]_2 \\ & [(\text{C}_3\text{H}_3)\text{Mo}(\text{CO})_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{3-x}\text{Bi}\text{Cl}_{1+x}] \ (x=0,1) \\ & [\text{Cp}_2\text{Mo}\{\text{Bi}(\text{OR})_2\}_2] \ (\text{R}=t\text{Bu}, \text{CH}(\text{CF}_3)_2) \\ & [\text{Me}\text{Cp}_2\text{Mo}\{\text{Bi}(\text{OB}u)_2\}] \ (\text{X}=\text{H}, \ \{\text{Bi}(\text{O}t\text{Bu})_2\}) \\ & [\text{R}\text{Cp}_2\text{Mo}\{\text{Bi}(\text{O}t\text{Bu})_2\}] \ (\text{X}=\text{H}, \ \{\text{Bi}(\text{O}t\text{Bu})_2\}) \\ & [\text{R}\text{Cp}_2\text{Mo}\{\text{Bi}(\text{O}t\text{Bu})\}_2 \ (\text{R}=\text{Me}, \text{H}) \\ & [(\text{Cp}*\text{MoO}_3)_2\text{Bi}(\theta-\text{toly}])_2]_n \\ & [\text{Bu}_4\text{N}]_2[(\text{MoO}_4)_2\text{Bi}\text{Ph}_3] \\ & [\text{Bu}_4\text{N}][(\text{Cp}*\text{MoO}_3)_2\text{Bi}(\theta-\text{toly}])_2] \end{split}$	Bi <sub>2</sub> O <sub>3</sub> , MoO <sub>3</sub>	[458] [447] [447] [149] [445,459] [446] [445,446] [450] [450] [448,449] [449]
$\begin{array}{l} Bi-V-O\\ [Cl_3BiV(O)(OC_2H_4OMe)_3]_2\\ [BiV(O)(sal)(Hsal)(salen')] \end{array}$	BiVO4 <sup>d</sup> , V2O5, Bi4V2O11 BiVO4	[431] [162]
Bi-M-O (M=Ni, Cu) [BiM(Hsal) <sub>3</sub> (salen)]		[162]
$Bi-M-O (M = Al, Co, V, Fe, Cr)$ $[Bi_2M(Hsal)_6M(acac)_3]$	$Bi_2Al_4O_9{}^d$ , $Bi_2O_3$ ; $Bi_4V_2O_{11}{}^d$	[430]
$Bi-M-O (M=Mn, Fe, Co, Ni, Cu, Zn)$ $[Bi_2M(hfac)_8]$		[432]
$Bi-M-O (M=Rh, Ru)$ $[BiM(O_2CCF_3)_4]$		[455]
$Bi-Ln-O \\ [(Bi_x Tb_{1-x} (O_2 C_2 H_2)_3 N] \cdot 2H_2 O \\ [NdBi(EDTA)(NO_3)_2] \cdot 7.22H_2 O \\ \end{tabular}$		[369] [441]

<sup>a</sup> Hydrolysis followed by pyrolysis of the amorphous material.

<sup>b</sup> 650 °C.

<sup>c</sup> 900 °C.

<sup>d</sup> Main product.

The molecular precursor depicted in Fig. 26 contains bismuth and titanium in a 1:2 molar ratio, and it might be anticipated that thermal decomposition should give  $Bi_2Ti_4O_{11}$ . However, complete decomposition upon heating to 600 °C gave an amorphous material, which upon sintering for 2 h at 750 °C gave  $Bi_4Ti_3O_{12}$  as the main crystalline product. The amount of the bismuth titanate  $Bi_2Ti_4O_{11}$  was estimated to be approximately 30% based on X-ray powder diffraction analysis. The formation of bismuth titanates starting from molecular single source precursors such as  $[BiTi_2O(OiPr)_9]$  was also investigated by Hubert-Pfalzgraf and coworkers [100]. The molecular structure of the trinuclear compound was determined by a single crystal X-ray diffraction analysis (Fig. 27) and reveals the connection of both atom types via metal–oxygen bonds. Such an arrangement is supposed to be advantageous for the formation of heterometallic oxides, because the two metal atom types are covalently linked in the molecular precursor. Indeed Bi<sub>2</sub>Ti<sub>4</sub>O<sub>11</sub> was observed upon hydrolysis of [BiTi<sub>2</sub>(O/Pr)<sub>9</sub>] followed by thermal treatment at 900 °C. However, decreasing the temperature to 650 °C for the thermal post-treatment afforded the pyrochlore structure Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>.

The same group provided another intriguing example. Thermal annealing of the amorphous hydrolysis product of  $[BiTi_2O(OEt)_9]$  at 1000 °C gave  $Bi_4Ti_3O_{12}$  as the major prod-



Fig. 26. Molecular structure of  $[Bi_2Ti_4(OiPr)(sal)_{10}(Hsal)(H_2O)]$  in the solid state [99]. The large black spheres correspond to Bi atoms and the large grey spheres to Ti atoms.

uct alongside Bi<sub>2</sub>Ti<sub>4</sub>O<sub>11</sub> as crystalline impurity. These results provide further evidence that the composition of the final material does not necessarily match the composition of the single source precursor, especially when additional hydrolysis steps are involved in the synthetic procedure. However, polycondensation of [Bi<sub>4</sub>Ti<sub>3</sub>O<sub>4</sub>(OEt)<sub>16</sub>] induced by hydrolysis and followed by thermal annealing at 450 °C gave the desired Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>. This result is remarkable because of the matching composition of precursor and heterometallic bismuth oxide and also because of the low crystallization temperature. Usually temperatures higher than 700 °C are required when mixtures of precursors such as  $[Bi(O_2CMe)_3]/[Ti(OC_2H_4OMe)_4], [Bi(OEt)_3]/[Ti(OnBu)_4]$ or [Bi(NO<sub>3</sub>)<sub>3</sub>]/[Ti(O*i*Pr)<sub>4</sub>] are used [427–429]. However, it should be noted that a proper choice of the precursors might give similar results as obtained by the use of a single source precursor. For example, a sol-gel process starting from a mixture of [Bi(OCH2CH2OMe)3] and [Ti(OCH2CH2OMe)4] following a spin-coating procedure and thermal annealing at 400–500 °C gave similar results when compared with the results obtained for the single source precursor [Bi<sub>4</sub>Ti<sub>3</sub>O<sub>4</sub>(OEt)<sub>16</sub>] [95].

In another approach, Whitmire and coworkers made use of the Lewis acidity of bismuth carboxylate complexes and the vari-



Fig. 27. Graphical representation of the molecular structure of  $[BiTi_2O(OiPr)_9]$  in the solid state [100].



Fig. 28. Graphical representation of the molecular structure of the heterobimetallic complex [ $\{Bi(Hsal)_3\}_2 \{Al(acac)_3\}$ ] in the solid state [430].

able coordination behaviour of bismuth. The pre-formed metal complexes  $M(acac)_3$  (acac = acetylacetonate) and M(salen) (salen = ethylenebis-salicylimine) prepared with the transition metals V, Cr, Fe, Co, Cr and the main group metal Al were coordinated to bismuth salicylate [Bi(Hsal)\_3] (H\_2sal = salicylic acid). Several of such heterometallic Lewis acid–Lewis base adducts have been prepared, characterized and their thermal decomposition analysed. Selected examples are given in Table 7 and the molecular structure of [{Bi(Hsal)\_3}\_2{Al(acac)\_3}] is depicted in Fig. 28.

The heterobimetallic complexes are easily prepared from [Bi(Hsal)<sub>3</sub>] and trivalent metal diketonate complexes of the type  $[M(acac)_3]$  (M = V, Al, Fe, Co, Cr) in a 2:1 molar ratio [430]. With exception of M = Co all complexes of the type  $[{Bi(Hsal)_3}_2 {M(acac)_3}]$  readily dissolve in non-coordinating solvents without disruption of their molecular integrity. In the case of M = Co a one-to-one complex was suggested to form in solution. All compounds have been studied by DTA/TGA and the residues were analysed using powder X-ray diffraction. The TGA traces typically show an onset temperature for the decomposition of approximately 180°C and in most cases end with an abrupt mass loss that occurs simultaneously with a strong exothermic event. The latter is assigned to the crystallization process of the corresponding heterometallic oxides. For the vanadium compound two such exothermic processes were observed. This is attributed to the stepwise oxidation of  $V^{3+}$  to  $V^{5+}$ . In case of [{Bi(Hsal)\_3}\_2{Al(acac)\_3}] the thermally induced decomposition gave a mixture of Bi2Al4O9 and the tetragonal phase of Bi<sub>2</sub>O<sub>3</sub>, whereas under identical conditions monoclinic Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> was obtained starting from  $[{Bi(Hsal)_3}_2 {V(acac)_3}]$  as the major crystalline phase with only a minor amount of impurity.

A similar synthetic approach was employed to study the thermolysis of the heterobimetallic complexes [Bi(Hsal)<sub>3</sub>Cu(salen)], [Bi(Hsal)<sub>3</sub>Ni(salen)] and [Bi(Hsal)(sal)-V(O)(salen')] [162]. The latter is of special interest as a single source precursor, because bismuth vanadates in general show a high oxide ion conductivity and photocatalytic activity. Pyrolysis of the bismuth-vanadium complex [Bi(Hsal)(sal)V(O)(salen')] gave almost pure monoclinic BiVO<sub>4</sub>. Similarly, the thermal decomposition of [BiCl<sub>3</sub>(O)V(OC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub> in an oxygen atmosphere gave BiVO<sub>4</sub> as main product together with some V<sub>2</sub>O<sub>5</sub> and Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> [431]. However with respect to oxide ion conduction the synthesis of the high-temperature phase of Bi<sub>2</sub>VO<sub>5.5</sub>  $(\gamma$ -phase) is highly desirable. It was shown previously that this phase is stabilized by the incorporation of a small amount of a second transition metal and that the transition metal-doped material shows a higher ion conductivity than the parent oxide. Such copper- and nickel-doped bismuth vanadates of the general formula  $Bi_2V_xM_{1-x}O_{5,5-\delta}$  were prepared by Whitmire and coworkers using mixtures of the above mentioned heterobimetallic salen complexes. Although these ternary metal oxides are also accessible via solid-state synthesis, the reaction temperature required for their preparation starting from mixtures of the heterobimetallic complexes is significantly reduced. Noteworthy, the thermal decomposition of pure [Bi(Hsal)<sub>3</sub>Ni(salen)] gave primarily the intermetallic phase BiNi<sub>3</sub> and a small amount of NiO nanoparticles [426]. The molecular structure of [Bi(Hsal)<sub>3</sub>Ni(salen)] is shown in Fig. 29.

Similarly to the approach reported by Whitmire and coworkers, Dikarev et al. recently reported the formation of heterobimetallic bismuth-transition metal  $\beta$ -diketonates through Lewis-acid/Lewis-base interactions [432]. They have prepared several homoleptic  $\beta$ -diketonates of the general formula [Bi<sub>2</sub>M(hfac)<sub>8</sub>] that contain the divalent transition metals



Fig. 29. Molecular structure of [Bi(Hsal)<sub>3</sub>Ni(salen)] in the solid state [162]. The large black sphere corresponds to the Bi atom and the smaller ones to carbon atoms; the large grey sphere corresponds to the Ni atom, while O and N atoms are represented by smaller spheres with different shades of grey from brighter to darker, respectively.

M = Mn, Fe, Co, Ni, Cu and Zn. The volatile compounds are readily soluble in coordinating solvents and thus might hold potential as single source precursors for heterometallic oxides or more likely oxyfluorides. Single crystal structure analyses revealed that in the trinuclear coordination compounds a planar [M(hfac)<sub>2</sub>] moiety is sandwiched between two [Bi(hfac)<sub>3</sub>] molecules. An oxygen atom of each [Bi(hfac)<sub>3</sub>] unit is coordinated to the central metal atom M, which thus is hexacoordinate. The bismuth atom adopts a distorted pentagonal pyramidal coordination.

Stavila et al. have reported several heterobimetallic bismuth coordination complexes with cobalt using EDTA as a chelating ligand for the large bismuth cation and studied their thermal decomposition [433-436]. The complexes are composed of a cationic complex containing the transition metal moiety and an anionic complex composed of the tetraanion of EDTA, a bismuth(III) cation and in some cases an additional ligand. All compounds that have been characterized by single crystal X-ray diffraction analysis were isolated as hydrates. Most interestingly, the majority of the hydrated complexes, namely trans-[Co(NH<sub>3</sub>)<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>][Bi(EDTA)(H<sub>2</sub>O)]<sub>2</sub>, [Co(NH<sub>3</sub>)<sub>4</sub>(CO<sub>3</sub>)][Bi(EDTA)], [CoL<sub>2</sub>D<sub>2</sub>]<sub>2</sub>[Bi(EDTA)(H<sub>2</sub>O)]<sub>2</sub> and  $[CoL_2(p-tol)_2]_2[Bi(EDTA)]_2$  (D = 1,2-cyclohexanedionedioximate; L = aniline; p-tol = para-toluidine) decompose upon thermal treatment to give the Sillenite-type phase  $Bi_{26-x}Co_xO_{40-\delta}$  and small amounts of  $Co_3O_4$  as crystalline material. The thermolysis of the copper bismuth EDTA complex [Cu(H<sub>2</sub>O)<sub>6</sub>][Bi(EDTA)]<sub>2</sub>·3H<sub>2</sub>O was reported by S. Sobanska et al. to yield Bi<sub>2</sub>CuO<sub>4</sub> as pyrolysis product [437]. Noteworthy, the molecular structures of bismuth-EDTA complexes with cationic main group metal moieties such as Ba[Bi(EDTA)<sub>2</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O and  $[Ca(H_2O)_7][Bi(EDTA)]_2 \cdot 2H_2O$  have also been reported [438,439].

#### 4.3. Bismuth/rare earth metal complexes

The bismuth(III) cation and the lanthanide(III) cations exhibit similar ionic radii, show high coordination numbers and a flexible coordination geometry. Despite the often cited stereochemical activity of the lone pair at the bismuth atom, it might be expected that both atom types adopt similar coordination geometries [394,440]. This should open up the possibility to assemble bismuth and lanthanide atoms within heterometallic single source precursors for mixed metal oxides with novel electrical or optical properties. Selected examples for such heterometallic oxides are Bi<sub>2-v</sub>Ln<sub>v</sub>Ru<sub>2</sub>O<sub>7</sub> [298-301],  $Bi_{2-x}Ln_xGeO_5$  (Ln = Y, Yb) [366] and Nd-doped  $Bi_{12}SiO_{20}$ [234–236]. These compounds were prepared using solid state reactions, and so far approaches with single source precursors are scarce. Examples of heterobimetallic complexes containing bismuth and lanthanides are restricted to carboxylates such as [NdBi(EDTA)(NO<sub>3</sub>)<sub>2</sub>]·7.22H<sub>2</sub>O [441] and  $[(Bi_xTb_{1-x})(O_2C_2H_2)_3N] \cdot 2H_2O$  [369]. The solid state structure of the latter is shown in Fig. 30. The single crystal X-ray structure analysis exhibits a polymeric chain structure isostructural with that reported for the homometallic bismuth nitriloacetate complex  $[Bi(O_2C_2H_2)_3N] \cdot 2H_2O$  [442]. Most interestingly, in



Fig. 30. Solid state structure of  $[(Bi_x Tb_{1-x})(O_2 C_2 H_2)_3 N] \cdot 2H_2 O[369]$ . The metal atoms are represented by black spheres, while C, N and O atoms are represented by different shades of grey from darker to brighter, respectively.

the heterobimetallic compound the bismuth and terbium atoms occupy the same position in the crystal lattice. Based on the calculated disorder model a bismuth to terbium ratio of 7:3 was suggested. The thermal decomposition of the complex was studied by DTA-TG, but unfortunately the thermolysis product was not investigated in detail. More detailed analyses of the decomposition products of diverse heterobimetallic bismuth/rare earth polyaminocarboxylates with Ln = La and Pr were reported by Devillers and coworkers [443].

Heterobimetallic bismuth/lanthanide alkoxides or siloxides were not reported so far. However, the molecular structures of [Bi(OSiMe<sub>3</sub>)<sub>3</sub>] and [Nd(OSiMe<sub>3</sub>)<sub>3</sub>] show a close structural relationship (Figs. 9 and 31), and it was suggested that heteronuclear bismuth/neodymium (oxo)siloxides might be accessible starting from these metal silanolates [394].

# 4.4. Bismuth/molybdenum compounds—SOHIO process and C–H activation

Among heterobimetallic bismuth-containing molecules those with molybdenum are of special interest, because they might serve as model compounds or as molecular precursors for the heterogeneous catalyst nMoO<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> (Table 1). The latter shows a high catalytic activity for the allylic oxidation of propene. The pure bimetallic oxide phase was used for the industrial production of acrolein until it was shown that other metal additives increase the selectivity and yield. Nowadays the simple heterobimetallic formulation is replaced by complex multicomponent catalysts, but there is strong evidence that the Bi/Mo oxide interface still provides the active sites for the catalytic cycle. The outstanding performance of the so-called SOHIOprocess (Standard Oil of Ohio Company) has stimulated much fundamental research on mechanistic aspects, but the mode of action even of the "simple" bimetallic nMoO<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> phase is still discussed controversially. A comprehensive overview on this topic is provided in two recent review articles [7,8]. The most important steps are propene coordination and activation, C–H activation and cleavage, and oxidation and C–O bond formation. Hanna and coworkers have recently reported that propene activation most likely involves Bi(III)–O bond homolysis to give Bi(II) radical species. Their observation was made upon attempts to prepare sterically hindered bismuth aryloxides by the salt metathesis route [444]. It turned out that the bismuth aryloxides of the type [Bi(OAr)<sub>3</sub>] (Ar = 2,6-R-C<sub>6</sub>H<sub>3</sub>, R = *i*Pr, *t*Bu) readily decompose and C–C coupling products were observed. It was suggested that these products result from homolytic Bi–OAr bond cleavage to give Bi(II) radicals and aryloxide radicals. The unusual reactivity of sterically hindered bismuth aryloxides is



Fig. 31. Molecular structure of  $[Nd(OSiMe_3)_3]$  [394] given for comparison with  $[Bi(OSiMe_3)_3]$  (Fig. 9). The large black spheres correspond to Nd atoms and the smaller ones to carbon atoms, while O and Si atoms are represented by different shades of grey from brighter to darker, respectively.



Fig. 32. Graphical representation of an organometallic bismuth oxo cluster formed upon intramolecular C–H activation ( $Ar = 2,6-iPr-4-Br-C_6H_2$ ) [8].

also demonstrated by the formation of the organometallic complex shown in Fig. 32. The bismuth oxo cluster was observed as a minor product upon the synthesis of [Bi(OAr)<sub>3</sub>] (Ar = 2,6-*i*Pr-4-Br-C<sub>6</sub>H<sub>2</sub>) following the alcohol–amide exchange route and demonstrates the potential of bismuth compounds for C–H activation [8]. Its molecular structure resembles that of the dimeric dibismuth oxo alkoxide [RBiOBiR]<sub>2</sub> (R =  $-C_6H_3$ -5-C(CH<sub>3</sub>)<sub>3</sub>-2-C(CF<sub>3</sub>)<sub>2</sub>O–) [356].

Noteworthy, an unusual C–F activation was observed upon attempts to prepare [Bi(OAr)<sub>3</sub>] (Ar = 2,4,6-CF<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>) by the reaction of BiCl<sub>3</sub> and NaOAr. Instead of the bismuth compound an ester of the formula ArOC<sub>6</sub>H<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>C(O)OAr was isolated in 40% yield. The sodium salt of the phenoxide is stable in solution and thus it was claimed that the presence of bismuth is crucial for this unexpected reaction to occur. The intermediate formation of [Bi(OAr)<sub>3</sub>] (Ar = 2,4,6-CF<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>) was suggested [350]. In contrast, the synthesis of [Bi(OAr)<sub>3</sub>] (Ar = 2,6-Me-C<sub>6</sub>H<sub>3</sub>) was reported by Evans et al. to proceed with 80% yield using the metathesis reaction [371]. In this case, no C–H activation was reported.

Additional examples of bismuth-induced intramolecular C–H activation were provided by Limberg and coworkers. They reported on unprecedented tetranuclear metal clusters with bismuth–carbon bonds which were obtained upon studies on heterobimetallic bismuth alkoxides containing a covalent bismuth–molybdenum bond [445,446]. The molecular structures of these unusual molybdenum–cyclopentadienide–bismuth complexes



Fig. 34. Graphical representation of heterometallic bismuth molybdenum alkoxides [149,447].

are shown in Fig. 33. They are formed by an intramolecular bismuth–carbon bond formation with release of *t*BuOH from dimeric [ $^{R}Cp_{2}Mo\{Bi(OtBu)\}$ ]<sub>2</sub> (R = Me, H) [445,446]. The unusual high reactivity (basicity) of the bismuth alkoxide moiety is explained on the basis of complex-induced proximity effects. The synthesis of one selected isomer starting from Cp<sub>2</sub>MoH<sub>2</sub> and [Bi(OtBu)<sub>3</sub>] is shown in Scheme 4 as an example. Along the reaction pathway compounds such as the labile monohydride [ $^{R}Cp_{2}MoH\{Bi(OtBu)_{2}\}$ ] (spectroscopic evidence only for R = Me) and the air- and moisture-sensitive metalla bismuth alkoxides [ $^{R}Cp_{2}Mo\{Bi(OtBu)_{2}\}$ ] and [ $^{R}Cp_{2}Mo\{Bi(OtBu)_{2}\}$ ] (R = Me, H) were observed.

Although in the  $nMoO_3/Bi_2O_3$  catalyst system no covalent bismuth–molybdenum bonds are present, these results demonstrate the potential of bismuth compounds for C–H activation, which is suggested as a fundamental process in the catalytic cycle of the allylic oxidation of propene. In recent years Limberg and coworkers have reported several other heterobimetallic Bi/Mo model compounds with implications for the SOHIO process. Among these compounds are heterobimetallic bismuth alkoxides with  $\pi$ -allyl molybdenum moieties such as those shown in Fig. 34. In these compounds the bismuth atoms are linked to molybdenum via oxygen atoms as is often assumed to be the case for the active sites in the Bi/Mo oxide phase.

However, in these complexes, the oxygen linkage is a result of  $\mu_2$ -bridging alkoxides rather than a result of a covalent Bi–O–Mo bond. Such covalent bonds have been reported by Klemperer and Liu in 1980 for the soluble complex [Bu<sub>4</sub>N]<sub>2</sub>[Ph<sub>3</sub>Bi(MoO<sub>4</sub>)<sub>2</sub>]·3H<sub>2</sub>O [448]. The compound contains molybdenum and bismuth in their highest oxidation states VI and V, respectively, but until recently, full characterization including a single crystal X-ray diffraction analysis was lacking. Limberg and coworkers have revisited Klemperer's work under



Fig. 33. Graphical representation of heterobimetallic bismuth molybdenum compounds formed upon C-H activation [445,446].



Scheme 4. Intramolecular C-H activation and C-Bi bond formation in heterometallic bismuth molybdenum alkoxides [445,446].

anaerobic conditions and they were able to isolate anhydrous  $[Bu_4N]_2[Ph_3Bi(MoO_4)_2]$  and to elucidate its molecular structure [449]. The coordination geometry at the bismuth atom is a slightly distorted trigonal bipyramid. Somewhat unexpected the Bi–O–Mo moieties are almost linearly arranged, which was explained by a highly ionic bond character and confirmed by DFT studies. However, the Bi–O bond length amounts to 2.169 Å, which is in the range expected for covalent Mo–O–Bi bonds. A different bonding situation was reported for the neutral complex [(Cp\*MoO\_3)\_2BiPh\_3], in which the dianionic subunit  $MoO_4^{2-}$  is replaced by the monoanionic ligand [Cp\*MoO\_3]<sup>-</sup> (Fig. 35) [450]. In this complex the Bi–O–Mo bond angles amount to 139.5° and 152.8°, and the Bi–O bond lengths to



Fig. 35. Graphical representation of the heterometallic Bi(V)–O–Mo(VI) compound [(Cp\*MoO<sub>3</sub>)<sub>2</sub>BiPh<sub>3</sub>] and the Bi(III)–O–Mo(VI) compound [(Cp\*MoO<sub>3</sub>){Bi(*o*-tolyl)<sub>2</sub>}]<sub>*n*</sub> [450].

2.198 and 2.204 Å. An NBO analysis supports a covalent bond character for the Mo–O–Bi bond.

A similar approach gave access to oxygen-bridged Mo(VI)/Bi(III) compounds. The reaction of [Bu<sub>4</sub>N][Cp\*MoO<sub>3</sub>] with [(o-tolyl)2Bi(hmpa)2]SO3CF3 provided the coordination polymer  $[(Cp*MoO_3){Bi(o-tolyl)_2}]_n$  that was characterized by a single crystal X-ray diffraction analysis [449,450]. Noteworthy, attempts to use Ph<sub>2</sub>BiBr as starting material failed as a result of the high Lewis-acidity of the diorganobismuth halide, which easily forms crystalline [Bu<sub>4</sub>N][Ph<sub>2</sub>BiBr<sub>2</sub>]. Further addition of [Bu<sub>4</sub>N][Cp\*MoO<sub>3</sub>] to the coordination polymer  $[(Cp*MoO_3){Bi(o-tolyl)_2}]_n$  provided the soluble complex  $[Bu_4N][(Cp*MoO_3)_2{Bi(o-tolyl)_2}]$  (Fig. 36) [449]. Remarkably, the heterobimetallic complexes are stable towards oxidation in air and hydrolysis by moisture. According to DFT calculations the Bi(III)-O-Mo(VI) bonds in [(Cp\*MoO<sub>3</sub>)<sub>2</sub>{Bi(o $tolyl_{2}]^{-}$  are of mainly covalent character, which is in contrast to the predominantly ionic character of the Bi(V)-O-Mo(VI) bonds in  $[Ph_3Bi(MoO_4)_2]^{2-}$ .

Within the family of heteropolyanions those containing bismuth in the oxidation state III, such as  $[Bi\{Mo_5-O_{13}(OMe)_4(NO)\}_2]^-$ ,  $[BiMo_6O_{21}(O_2CCH_2NH_3)_3]^{3-}$  or  $[Bi_2W_{22}O_{74}(OH)_2]^{12-}$  have been reported [451–454]. The relevance of such metal oxo clusters containing oxygen-bridged M(VI)/Bi(III) units as model compounds for example for the allylic oxidation of propene in the SOHIO process is limited. In these compounds the bismuth atom is deeply buried within the metal oxo cage and thus is not accessible.

Another question concerning the SOHIO process still under debate is whether bridging oxygen atoms between bismuth and molybdenum are necessary at all for the oxygen transfer reaction. Limberg and coworkers have used the heterobimetallic complex [(C<sub>3</sub>H<sub>5</sub>)Mo(CO)<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>3</sub>BiCl] as a single source precursor for a heterobimetallic bismuth molybdenum oxo catalyst (Fig. 34) [149]. The compound was reacted with silica and calcined to give nanometer-sized bismuth oxo clusters



Fig. 36. Synthesis of the soluble complex [Bu<sub>4</sub>N][(Cp\*MoO<sub>3</sub>)<sub>2</sub>{Bi(o-tolyl)<sub>2</sub>}] [445].

together with low-nuclearity molybdenum oxo particles spread over the silica surface. Thus, segregation has taken place. However, this material is still active in the oxidation of propene to acrolein, although the conversion efficiency is low. The authors conclude that bismuth and molybdenum are essential for the allylic oxidation of propene, but they have doubts about the hypothesis that both atom types have to be linked covalently as part of a bismuth molybdate compound. It seems to be sufficient when bismuth oxo clusters are present to initiate the C–H bond abstraction. The molybdenum species that are located close to these clusters trap and convert the ally radicals. Most likely, the bismuth molybdate – if present – allows for a fast reoxidation of the catalyst surface.

In summary, there is still much research left to gain a better insight into the mechanistic details of the SOHIO process. Having in mind that multicomponent catalysts are now used in the industrial process it is rather challenging to get a deeper knowledge of the actual catalytic cycle.

## 4.5. Carboxylates containing a metal-bismuth bond

In addition to the bismuth compounds with Bi-Mo bonds reported here a large variety of heterobimetallic compounds with bismuth-metal bonds have been described in the literature [9]. This review will only focus on a few selected examples containing carboxylate ligands. Such compounds have been reported recently and might serve as single source precursors to heterometallic oxides. Heterobimetallic carboxylates such as  $[BiRh(O_2CCF_3)_4]$  and  $[BiRu(O_2CCF_3)_4]$  were obtained upon heating stoichiometric mixtures of  $[Bi_2(O_2CCF_3)_4]$  and  $[M_2(O_2CCF_3)_4]$  (M = Rh, Ru) [455]. The molecular structures of these heterobimetallic compounds show paddle-wheel units with both atom types adopting a distorted square pyramidal coordination geometry. Similar to  $[Bi_2M(hfac)_8]$  (M = Mn, Fe, Co, Ni, Cu and Zn) [432] additional Lewis-acid-Lewis-base interactions involving the transition metal and an oxygen atom from a ligand coordinated to bismuth are observed. The bismuth atoms do not show any intermolecular coordination. Thus a one-dimensional coordination polymer results in the solid state (Fig. 37). Noteworthy, the solvent-free analogous homometallic bismuth(II) trifluoroacetate does not show any intermolecular bismuth oxygen coordination either [456]. This very unusual bismuth compound was first reported by Frank et al. [378]. They obtained [Bi<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>] upon thermolysis of [Bi(O<sub>2</sub>CCF<sub>3</sub>)<sub>3</sub>] in the presence of hexamethylbenzene in a sealed tube with approximately 20% yield. The compound was isolated in form



Frank 1998

Fig. 37. Graphical representation of the polymeric structures of [BiRu- $(O_2CCF_3)_4$ ] and [Bi<sub>2</sub>( $O_2CCF_3$ )<sub>4</sub>]·C<sub>6</sub>Me<sub>6</sub> [378,455].

of its C<sub>6</sub>Me<sub>6</sub> adduct, which forms a one-dimensional coordination polymer through Bi– $\pi$  arene coordination (Fig. 37). In 2004 Dikarev and Li were able to improve the yield and developed a more sophisticated synthetic protocol for [Bi<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>], which is based on the comproportionation of elemental bismuth and bismuth(III) trifluoroacetate [456]. Recently, the synthesis and X-ray single crystal structure analysis of novel mixed ligand bismuth–rhodium carboxylates such as [*cis*-BiRh(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(O<sub>2</sub>CtBu)<sub>2</sub>] and [BiRh(O<sub>2</sub>CCF<sub>3</sub>)<sub>3</sub>(O<sub>2</sub>CMe)] starting from bismuth(III) trifluoroacetate were also communicated [457].

## 5. Conclusion and outlook

Metal oxides play a major role in the growing microelectronics industry and there is therefore an ongoing search for novel metal oxide-based materials as well as for improved synthetic strategies for well-established products. Bismuth-containing oxides have been shown to offer a variety of interesting physical properties such as superconductivity, ferroelectricity and ferromagnetism. The latter two are useful for the development of next generation storage media and are strongly influenced by the nature of the metal-oxo interaction. A unique feature of bismuth is its unusual coordination chemistry, which often leads to unsymmetric geometries. Thus, solid state structures often display strong distortions, possibly giving rise to anisotropic physical properties. An interesting class of materials is that of the so-called multiferroics, which show simultaneously ferromagnetic, ferroelectric and/or ferroelastic long-range ordering. Bismuth-containing oxides such as BiFeO3 are among the most promising candidates for such multiferroic materials. However, not only the search for novel materials but also the quest for novel mild synthetic procedures is becoming of utmost importance. Having in mind the miniaturization of devices down to the  $\mu$ m and nm scale, the conventional solid state reactions are more and more replaced by modern synthetic approaches such as improved sol-gel and (liquid injection) MOCVD processes. The latter can be better adapted to microfabrication of devices and allows a better control of interfacial properties. However, these synthetic routes require more sophisticated metal-containing precursors, which are so far scarce for bismuth. The development of single source precursors for bismuth-containing heterometallic oxides is still in its infancy. Recent approaches in this direction have shown that bismuth alkoxides and carboxylates seem to be the most promising candidates. Bismuth siloxides show a strong tendency to give bismuth silicates, but they offer a better control of the solubility even of larger aggregates.

For the ongoing miniaturization it is important to get a deeper insight into the stepwise growth of metal oxo particles. Control over the growth process of metal oxo/hydroxo clusters is a key step to control the morphology and physical properties of the final material. Recent studies on several structurally related bismuth oxo clusters provided a first look at the hydrolysis and polycondensation process of bismuth compounds. Bismuth oxo siloxides with up to fifty bismuth atoms were detected and it is to be expected that even larger aggregates will become accessible. These studies are at the beginning and much more data must be collected. First results show that the hydrolysis/polycondensation process follows a simple Aufbau principle, that is the f.c.c.-assembly of bismuth atoms and primarily occupation of tetrahedral voids by oxygen atoms. However, occupation of octahedral voids was also observed in some cases, but due to limited data could not be finally assessed. The large bismuth oxo siloxides serve as model compounds, but in principle they might also offer the possibility of surface functionalization, since the Bi-OSiR<sub>3</sub> bond is easily cleaved by organic acids.

Bismuth oxide-containing materials have long been used as heterogeneous catalysts for example in combination with molybdenum oxide for the oxidation of propene to give acrolein and the ammoxidation of propene to acrylonitrile. Recently, the activation of C–H bonds by heterobimetallic bismuth alkoxides was reported and this finding might initiate the search for novel bismuth oxide-based catalysts. The latter might be classified as environmentally benign, since bismuth is often termed a non-toxic element. However, there is still some ongoing debate about the toxicity of certain bismuth compounds. In this context, it should be stated that generally speaking the term non-toxic itself is misleading. However, bismuth compounds show a significantly reduced toxicity compared to structurally related compounds containing arsenic, antimony or heavy metals such as Sn, Pb, Tl, Hg and Cd. The aspect of low toxicity will play a major role in future materials design and thus bismuthcontaining materials might attract increasing interest also from this point of view. However, the main focus in future work is expected to concentrate on the development of novel bismuth oxide-based functional materials. Thus, there is much need for novel and more sophisticated molecular precursors that match the requirements of modern materials synthesis.

# Note added in proof

After this manuscript was edited two fascinating giant homometallic bismuth oxo clusters were reported, namely  $[Bi_{38}O_{45}(hfac)_{24}]$  (hfac = hexafluoroacetylacetonate) (E. V. Dikarev, H. Zhang, B. Li, Angew. Chem. Int. Ed. 45 (2006) 5448) and [Bi<sub>38</sub>O<sub>44</sub>(Hsal)<sub>26</sub>(Me<sub>2</sub>CO)<sub>16</sub>(H<sub>2</sub>O)<sub>2</sub>] (P.C. Andrews, G.B. Deacon, C.M. Forsyth, P.C. Junk, I. Kumar, M. Maguire, Angew. Chem. Int. Ed. 45 (2006) 5638). We recently observed a very similar compound, [Bi<sub>38</sub>O<sub>45</sub>(OTf)<sub>24</sub>] [422]. These bismuth oxo clusters match with the Aufbau Principle based on edge-sharing Bi<sub>6</sub> units as described in Fig. 21, although slightly different metal oxo cores are reported. Additionally, novel bismuth compounds of the type  $[(o-tolyl)_2BiOR]$  (R = Me, H) (S. Roggan, C. Limberg, B. Ziemer, M. Siemons, U. Simon, Inorg. Chem. in press) and [BiL]  $(H_3L = tris(3,5-dimethy)^{-2})$ hydroxybenzyl)amine) (L.E. Turner, M. G. Davidson, M.D. Jones, H. Ott, V.S. Schulz, P.J. Wilson, Inorg. Chem. 45 (2006) 6123) were recently reported.

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