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Structural Relationships in High-Nuclearity Heterobimetallic Bismuth-Oxo Clusters

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The novel heterobimetallic sodium-bismuth-oxo clusters $[Bi_2Na_4O(OSiMe_3)_8]$ (**1**), $[Bi_{10}Na_5O_7(OH)_6(OSiMe_3)_{15}]\cdot 1.5C_7H_8$ (**2**·$1.5C_7H_8$), $[Bi_{15}Na_3O_{18}(OSiMe_3)_{12}]\cdot C_7H_8$ (**3**·C_7H_8) and $[Bi_{14}Na_8O_{18}(OSiMe_3)_{14}(THF)_4]\cdot C_6H_6$ (**4**·C_6H_6) were prepared starting from $BiCl_3$ and $NaOSiMe_3$. Compound **1** crystallises in the trigonal space group $R\bar{3}c$ with the lattice constants a = 12.8844(3) Å and c = 54.6565(3) Å, compound **2**·$1.5C_7H_8$ crystallises in the triclinic space group $P\bar{1}$ with the lattice constants a = 15.0377(2) Å, b = 16.0373(2) Å, c = 27.8967(5) Å, α = 87.1321(6)°, β = 86.6530(7)° and γ = 63.6617(6)°, compound **3**·C_7H_8 crystallises in the monoclinic space group $C2/c$ with the lattice constants a = 54.311(11), b = 19.846(4), c = 22.885(5) Å and β = 112.32(3)°, and compound **4**·C_6H_6 crystallises in the trigonal space group $R\bar{3}$ with the lattice constants a = 15.9786(4) Å and c = 46.8329(17) Å. The formation of M–O–M bonds results from both partial hydrolysis followed by condensation as well as from elimination of $Me_3SiOSiMe_3$ from M–$OSiMe_3$ groups. The hexanuclear metal-oxo silanolate **1** is more conveniently synthesised by the addition of $NaOSiMe_3$ to a toluene solution of in situ-prepared $[Bi(OSiMe_3)_3]$. The metal-oxo(hydroxo) silanolates differ significantly in composition, but show similar building units. Thermal decomposition of the metal-oxo silanolates in the solid state gave heterogeneous decomposition products containing bismuth silicates.

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Introduction

Bismuth alkoxides are valuable precursors for the synthesis of bismuth oxide-based materials prepared via chemical vapour deposition[1] or via the sol-gel process.[2,3] Their potential application for the synthesis of materials such as high-temperature superconductors or non-volatile random-access memories has prompted several research groups to investigate the reactivity and the structural chemistry of homo- and heterometallic bismuth alkoxides in order to control composition and morphology of the final material on a molecular level.[3–6] Alternatively, bismuth silanolates might serve as molecular precursors to bismuth-containing materials. However, the chemistry of bismuth silanolates was only scarcely explored so far.[7–11] In contrast to bismuth, metallasiloxanes of the heavier group 14 metals tin and lead have received considerable interest.[7,8,12,13] It was noticed that homoleptic heavy metal silanolates of the type $[M(OSiR_3)_2]$ (M = Sn, Pb) readily decompose at moderate temperatures with elimination of $R_3SiOSiR_3$ to give the parent metal oxide or metal-oxo clusters.[7,13] It is promising to exploit this non-hydrolytic strategy for the synthesis of tailor-made bismuth-oxo clusters and bismuth oxide-based nanoparticles. Recently, the potential of metal silanolates as molecular precursors for a variety of mixed metal oxide materials[8,14] as well as for nanoparticles of zinc oxide[15] and zinc silicate[16] was demonstrated.

Among the homoleptic bismuth silanolates the trimethylsilyl derivative $[Bi(OSiMe_3)_3]$ is one of the most promising candidates with respect to materials synthesis. The reaction of $BiCl_3$ with $NaOSiMe_3$ was previously reported to give $[Bi(OSiMe_3)_3]$,[7] but the material obtained gave analytical data which disagreed with the expected values. We have revisited this reaction and report here our findings including the molecular structures of $[Bi_2Na_4O(OSiMe_3)_8]$ (**1**), $[Bi_{10}Na_5O_7(OH)_6(OSiMe_3)_{15}]\cdot 1.5C_7H_8$ (**2**·$1.5C_7H_8$), $[Bi_{15}Na_3O_{18}(OSiMe_3)_{12}]\cdot C_7H_8$ (**3**·C_7H_8), and $[Bi_{14}Na_8O_{18}(OSiMe_3)_{14}(THF)_4]\cdot C_6H_6$ (**4**·C_6H_6).

Results and Discussion

Reaction of $NaOSiMe_3$ with $BiCl_3$ in a 3:1 stoichiometry using THF as solvent gave a solid material the EDX analysis of which accounted for the presence of both bismuth and sodium. Crystallisation from hot toluene gave single crystals of the heterometallic bismuth-oxo silanolate $[Bi_2Na_4O(OSiMe_3)_8]$ (**1**). The low yield was only slightly improved to approximately 10% when the reaction was carried out in toluene and the stoichiometry was modified to a bismuth-to-sodium ratio of 1:5 (Scheme 1).

Oxygen incorporation into compound **1** does not result from hydrolysis, but from the reaction of M–$OSiMe_3$ groups to give $Me_3SiOSiMe_3$ and the corresponding metal-

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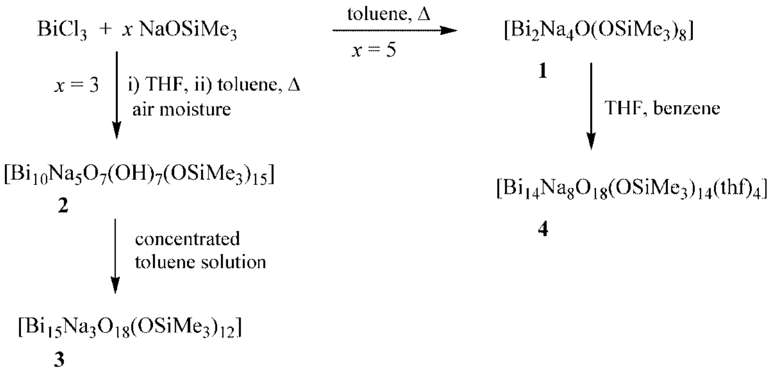

Scheme 1.

oxo fragment. The ^{29}Si NMR spectrum of a crude reaction mixture according to Scheme 1 (x = 5) showed a signal at δ = 7.2 ppm assigned to $Me_3SiOSiMe_3$ and a broad signal at δ = –2.9 ppm assigned to unreacted $NaOSiMe_3$. Due to its poor solubility, no ^{29}Si NMR signal was observed for $[Bi_2Na_4O(OSiMe_3)_8]$ (**1**). Compound **1** was obtained with a significantly higher yield when in situ-prepared $[Bi(OSiMe_3)_3]$ (^{29}Si NMR δ = 10.9 ppm) and $NaOSiMe_3$ were used as starting materials [Equation (1)]. The synthesis and molecular structure of $[Bi(OSiMe_3)_3]$ was reported recently.[11b]

$$2\,[Bi(OSiMe_3)_3] + 4\,NaOSiMe_3 \xrightarrow[\text{toluene}]{-\,Me_3SiOSiMe_3} \underset{\mathbf{1}}{[Bi_2Na_4O(OSiMe_3)_8]} \qquad (1)$$

The molecular structure of compound **1** is best described to be composed of an octahedron with two bismuth atoms and four sodium atoms occupying the corners and a μ_6-oxygen atom being enclosed within the octahedron (Figure 1). Eight silanolate groups cap the trigonal faces. The compound crystallises in the space group $R\bar{3}c$ and only one crystallographic independent position for the metal atoms is found. Each position is occupied by both sodium and bismuth atoms with occupancies of 2/3 and 1/3, respectively. The analogous problem of disorder was reported for the closely related molecular structures of $[Sb_2Na_4O(OSiMe_3)_8]$,[17] $[Bi_2Na_4O(O\mathit{t}Bu)_8]$,[18] $[Sb_2M_4O(O\mathit{t}Bu)_8(thf)_n]$ (M = Na, n = 0; M = K, n = 0, 4),[18] and $[Bi_2Na_4O(OC_6F_5)_8(thf)_4]$.[19] For these compounds it was shown by means of solid state NMR, variable-temperature NMR in solution and crystallography that both in the solid state and in solution the group 15 atoms are located in *cis*-position of the octahedron. We have carried out a theoretical study of *cis*- and *trans*-$[Bi_2Na_4O(OSiMe_3)_8]$ (**1**) at the RHF/LANL2DZ level of theory which confirms that a *cis*-arrangement is favoured ($\Delta E_{cis/trans}$ = 3.92 kcal mol^{-1}). At room temperature only one ^{1}H NMR signal is observed for the methyl protons, which is indicative of a fast exchange process involving the trimethylsilanolate groups. Further NMR studies in solution, such as variable temperature NMR, were hampered by the low solubility of compound **1**.

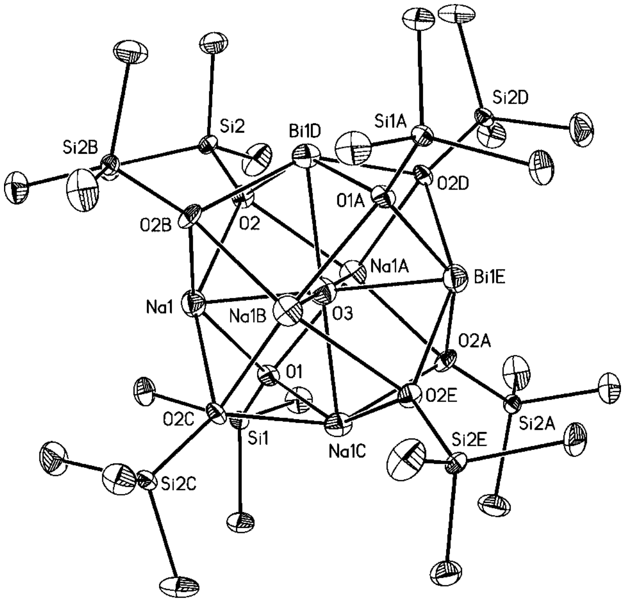

Figure 1. ORTEP diagram of $[Bi_2Na_4O(OSiMe_3)_8]$ (**1**) showing 30% displacement ellipsoids and the atom numbering scheme. Hydrogen atoms are omitted. The positions of the metal atoms are occupied by both sodium and bismuth atoms with occupancies of 2/3 and 1/3, respectively. Selected bond lengths [Å] and bond angles [°] (M = Na, Bi): M(1)–O(3) 2.289(1), M(1)–O(2) 2.361(2), M(1)–O(2B) 2.422(2), M(1)–O(2C) 2.405(2), M(1)–O(1) 2.361(2); M(1)–O(3)–M(1E) 180.00(1), M(1)–O(3)–M(1B) 89.55(1), M(1)–O(3)–M(1C) 90.45(1), M(1)–O(2)–M(1A) 84.88(5), M(1)–O(2B)–M(1D) 84.61(5), M(1)–O(1)–M(1C) 86.11(8), O(1)–M(1)–O(2) 86.39(4), O(1)–M(1)–O(3) 73.56(5), O(2)–M(1)–O(3) 74.51(4), O(2)–M(1)–O(2B) 86.09(4), O(2)–M(1)–O(2C) 147.06(7). Symmetry operations used to generate equivalent atoms: A = $-y, x-y, z$; B = $y, -x+y, -z$; C = $-x+y, -x, z$; D = $x-y, x, -z$; E = $-x, -y, -z$.

The reaction of $BiCl_3$ with $NaOSiMe_3$ in 1:3 stoichiometry according to Scheme 1 gave a solid material containing sodium, bismuth and silicon as was shown by EDX analysis. The ^{29}Si NMR spectrum of the supernatant solution showed only one signal assigned to $Me_3SiOSiMe_3$. Crystallisation from toluene gave a crop of single crystals of the novel heterobimetallic compound of the formula [Bi$_{10}$-

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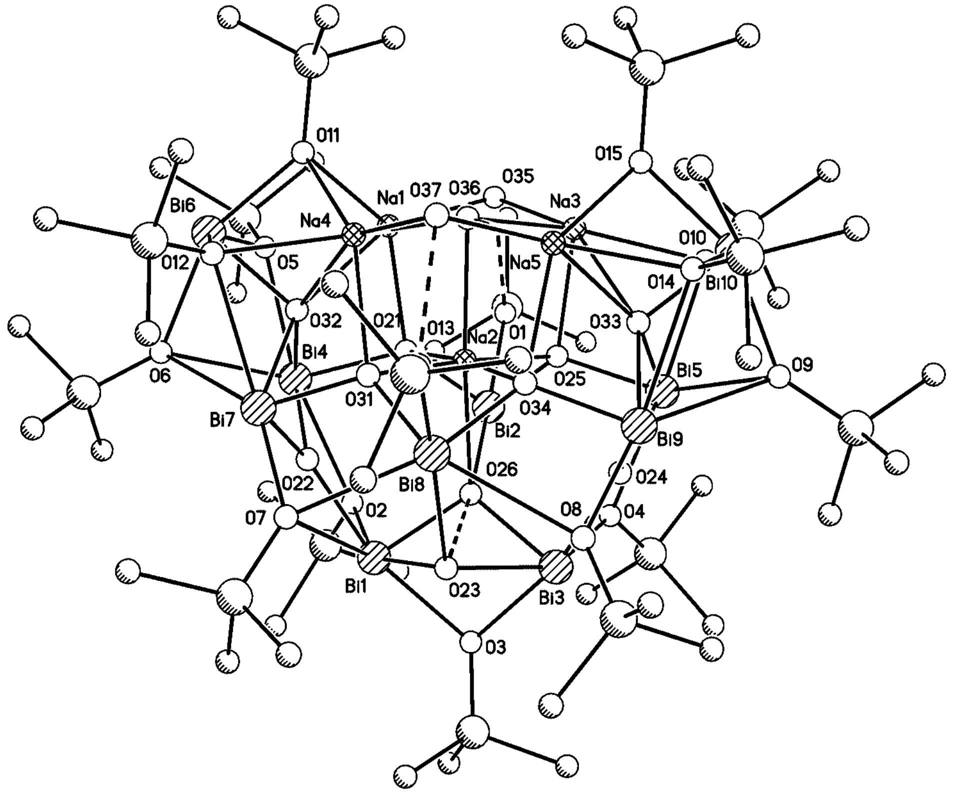


Figure 2. Molecular structure of $[Bi_{10}Na_5O_7(OH)_6(OSiMe_3)_{15}]$ (**2**); hydrogen atoms are omitted; typical bond lengths [Å] and bond angles [°] are found in the ranges: Bi–O 2.056(4)–2.728(5), Na–O 2.369(4)–2.710(5); O–Bi–O 64.5(2)–98.8(2) and 128.0(2)–166.5(2), O–Na–O 62.0(2)–99.2(2) and 122.1(2)–156.7(2), O–Na(2)–O 65.4(2)–106.3(2) and 112.6(2)–175.9(2), Bi–O–Bi 84.9(2)–137.1(2), Bi–O–Na 79.4(2)–158.7(2), Na–O–Na 79.9(2)–168.3(2). Additionally, weak secondary bonds between bismuth and oxygen with distances of 3.0 Å are observed for Bi(7) and Bi(9).

$Na_5O_7(OH)_6(OSiMe_3)_{15}]\cdot 1.5C_7H_8$ (**2**$\cdot 1.5C_7H_8$) (Figure 2). Apparently, partial hydrolysis of initially formed compounds took place as a result of contact with air moisture. Noteworthy, formation of single crystals of the metal oxo cluster **2** were also observed when a C_6D_6 solution of "$[Bi(OSiMe_3)_3]$", prepared from $NaOSiMe_3$ and $BiCl_3$, was kept for approximately two weeks under atmospheric conditions. We recently noticed, that reaction of $BiCl_3$ with $NaOSiMe_3$ (ratio 1:3) at room temperature under rigorous exclusion of air moisture again produced compound **1** as major product, but additionally single crystals of the bismuth-oxo silanolates $[Bi_{18}Na_4O_{20}(OSiMe_3)_{18}]$ and $[Bi_{33}NaO_{38}(OSiMe_3)_{24}]$ were obtained from toluene/benzene. A detailed comparison of the molecular structures of these bismuth-rich compounds with polynuclear homometallic bismuth-oxo silanolates is reported elsewhere.[11c] In conclusion, $[Bi_2Na_4O(OSiMe_3)_8]$ (**1**) is always obtained as the major product by the metathesis route and subtle changes regarding temperature, moisture and choice of the solvent lead to various heterobimetallic oxo(hydroxy)silanolates as byproducts.

The molecular structure of $[Bi_{10}Na_5O_7(OH)_6(OSiMe_3)_{15}]$ (**2**) is shown in Figure 2 and selected bond lengths and bond angles are given in the Figure caption. Compound **2** is composed of a metal-oxo core comprising 15 metal atoms and 15 trimethylsilyl groups. The metal-oxo core is best described to be composed of the different subunits **A**, **A′** and **B**, which are connected via Na(2) placed in the centre of the metal-oxo core (Figure 3). At the periphery of the molecule a total of fifteen μ_2- and μ_3-silanolate groups is found.

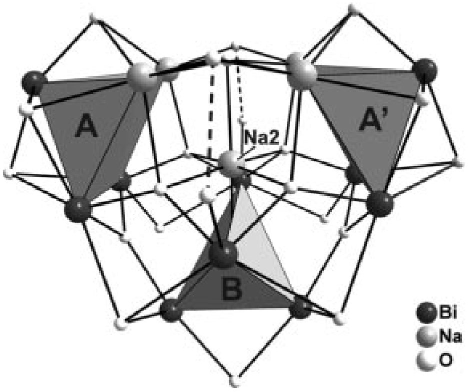


Figure 3. View of the $[Bi_{10}Na_5O_{28}]$ core structure of compound **2** (Me_3Si groups and H atoms are omitted; six oxygen atoms are covered by polyhedra). The sodium atom Na(2) connects the fragments **A**, **A′** and **B**.

Both pentanuclear fragments **A** and **A′** are composed of three bismuth atoms, two sodium atoms and thirteen oxygen atoms. The five metal atoms occupy the corners of a square pyramid with four μ_3-silanolate groups capping each trigonal face (Figure 4). A μ_5-oxygen atom occupies approximately the centre of the basal plane. In addition, four oxygen atoms are coordinated terminal to the metal atoms of the basal plane of **A** and four oxo ligands are bidentate bridging. The subunits **A** and **A′** are not related by symmetry, but show similar bond lengths and bond angles. The basic structural motif of the [$Bi_3Na_2O_{13}$] fragment **A** is closely related to the metal-oxo core of [$Bi_2Na_4O(OSiMe_3)_8$] (**1**) as is shown in Figure 4. Other examples with related molecular structures were reported among pentanuclear metal μ_5-oxo alkoxides,[20,21] several hexanuclear compounds with μ_6-oxo ligands[17–19,21,22] and hexanuclear bismuth-oxo-hydroxo cations with a [Bi_6O_8] fragment (Figure 4).[23]

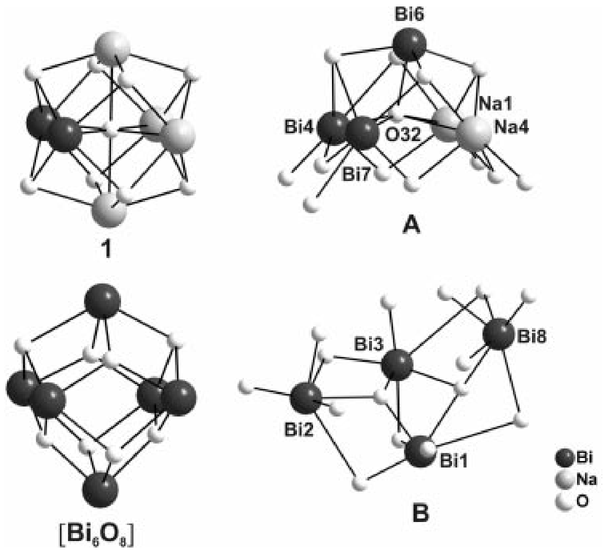
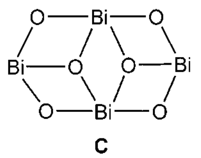


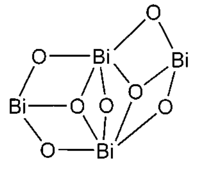
Figure 4. View of the structural fragments, which constitute the metal-oxo clusters **1**, **2** (**A** and **B**) and the [Bi_6O_8] fragment of previously described hexanuclear bismuth-oxo-hydroxo cations.[23]

In compound **1** the oxygen atom is located in the centre of the cluster and thus all M–O (M = Na, Bi) bond lengths equally amount to 2.289(1) Å. This is a result of the disorder model suggested for the symmetric cluster **1**. In contrast, fragment **A** shows two short Bi–μ_5-O distances [Bi(4)–O(32) 2.192(4) Å, Bi(6)–O(32) 2.086(4) Å], a longer Bi–μ_5-O bond length [Bi(7)–O(32) 2.425(4) Å] and two similar Na–μ_5-O distances [Na(1)–O(32) 2.559(5) Å, Na(4)–O(32) 2.588(5) Å]. However, the average M–μ_5-O distance in **A** (av. M–O 2.365 Å) is close to the M–O distance in compound **1**. Comparison of the metal-oxo core structure of **1** with that of **A** sheds some light on the disorder problem reported above for compound **1**. The higher oxophilicity of the bismuth atom compared with the sodium atom should favour the formation of short Bi–O distances to give a *cis*-arrangement in compound **1** as it was observed for subunit **A**. This result is in agreement with our theoretical model. A *cis*-arrangement gives a structure of lower symmetry. Thus, we suggest the disorder observed in compound **1** to be a result of disordered molecules in the crystal lattice rather than disordered metal atoms. Noteworthy, another example, namely [$(Cp^*Zr)_6(\mu_4\text{-}O)(\mu_2\text{-}O)_4(\mu_2\text{-}OH)_8$], was reported recently, in which an asymmetric structure with an μ_4-oxo ligand in the centre of an octahedron is favoured over the more symmetric structure which requires an ideal μ_6-oxo ligand.[24]

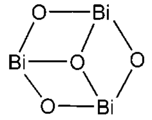
The structural fragment **B** consists of four bismuth atoms and fifteen oxygen atoms (Figure 4). The [Bi_4O_{15}] fragment resembles the Bi_4O_6-ladder-type arrangement (**C**) which was described as a central structural motif in other bismuth-oxo compounds.[6,25] However, in contrast to the ladder-type arrangement **C** fragment **B** is strongly distorted and an additional μ_2-oxo ligand connects the two central bismuth atoms to give an structural arrangement, which is better assigned to type **C′**. Molecular structures based on this motif have been reported for the bismuth-oxo alkoxides [$Bi_6O_3(OR)_{12}$] (R = C_6F_5,[6] 2,6-$C_6H_3Cl_2$[26]). Both structural arrangements **C** and **C′** can formally be reduced to the trinuclear fragment **D**, which might be expected to be the most stable building unit of bismuth-oxo clusters. However, so far discrete trinuclear units similar to type **D** were solely observed for hydrolysis products of bismuth trifluoroacetate, such as [$Bi_3(OH)(OOCCF_3)_8$].[23k,27]



C



C'



D

The more symmetric ladder-type arrangement **C** is observed for the central metal-oxo core composed of Bi(7)–Bi(9) and Na(2) (Figure 5). Each bismuth atom belongs to a different subunit [Bi(7) in **A**, Bi(9) in **A′** and Bi(8) in **B**; see Figure 3 and Figure 4] which are connected by Na(2).

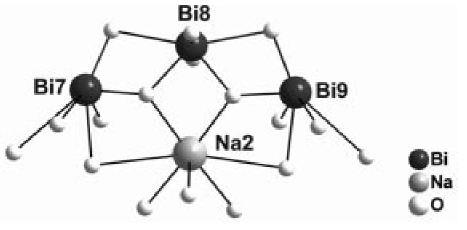


Figure 5. View of the central metal-oxo core of compound **2**, which connects the three subunits **A**, **A′** and **C**.

The heavy metal bismuth in [$Bi_{10}Na_5O_7(OH)_6(OSiMe_3)_{15}$]·1.5$C_7H_8$ (**2**·1.5C_7H_8) does not unambiguously allow the location of OH hydrogen atoms. However, different O···O distances make an assignment of hydroxy groups possible. Thus, O(35) [O(35)···O(1) 2.618(7) Å], O(37) [O(37)···O(13) 2.680(7) Å], O(23) [O(23)···O(26) 2.564(6) Å], O(22) [O(22)···O(2) 2.766(7) Å], and O(24) [O(24)···O(4) 2.783(7) Å] are assigned to hydroxo ligands. In addition, we suggest O(36), which is located at the periphery of the metal-oxo silanolate, to be a hydroxo ligand.

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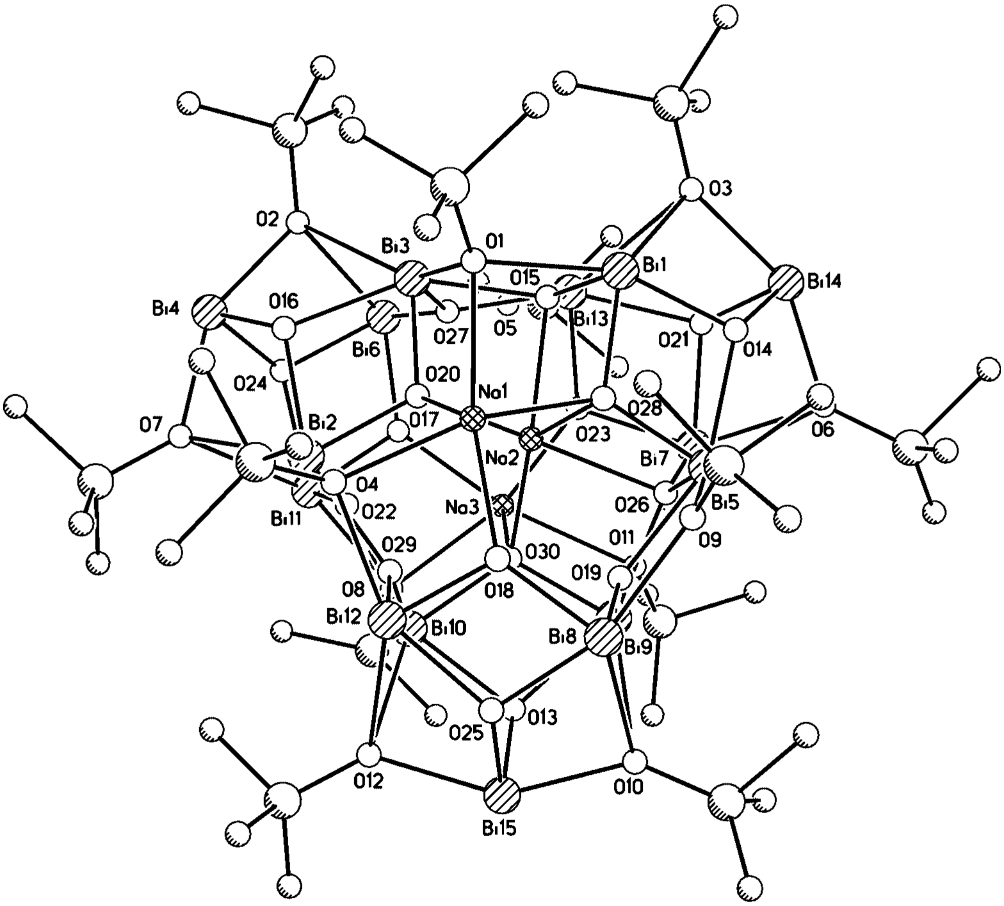

Figure 6. Molecular structure of $[Bi_{15}Na_3O_{18}(OSiMe_3)_{12}]$ (**3**); hydrogen atoms are omitted; typical bond lengths [Å] and bond angles [°] are found in the following ranges: Bi–O 2.033(9)–2.737(9), Na–O 2.264(10)–2.606(12); O–Bi–O 64.9(3)–160.1(3), O–Na–O 70.1(3)–165.1(4), Bi–O–Bi 93.9(3)–134.3(4), Bi–O–Na 84.6(3)–138.0(4). Additionally, weak secondary bonds between bismuth and oxygen with distances in the range of 3.2–3.5 Å are observed for Bi(2), Bi(5), Bi(9) and Bi(11)–Bi(13).

After the batch of single crystals of $\mathbf{2}\cdot1.5C_7H_8$ had been separated by filtration, a second crystal fraction, hereafter referred to as $\mathbf{3}\cdot C_7H_8$ (Figure 6), was obtained. The molecular structure of $[Bi_{15}Na_3O_{18}(OSiMe_3)_{12}]\cdot C_7H_8$ ($\mathbf{3}\cdot C_7H_8$) is closely related to that of compound **2** although both compounds differ significantly in composition. The metal-oxo core of compound **3** is best described to be composed of three $[Bi_5O_{12}]$ subunits of type **E**, which are connected via three sodium atoms (Figure 7). Each subunit **E**, **E′** and **E′′** shares four oxygen atoms with a neighbouring subunit. The $[Bi_5O_{12}]$ subunits **E**, **E′** and **E′′** show similar structural parameters and thus only **E** is discussed in more detail (Figure 8).

The $[Bi_5O_{12}]$ subunit **E** is composed of five bismuth atoms, which occupy the corners of a square pyramid (Figure 8). Two μ_3-silanolate groups and two μ_3-oxygen atoms cap the trigonal faces. Each bismuth atom of the basal plane is connected to two bismuth atoms of the same plane by two oxo ligands. These oxo ligands further link each subunit to another subunit and/or a sodium atom to give six μ_3- and six μ_4-oxo ligands. In addition, six silanolate groups bridge adjacent corners of two subunits. Four of these ligands additionally coordinate to a sodium atom, which results in four μ_3- and two μ_2-OSiMe$_3$ ligands. Noteworthy, the molecular structures of the recently reported nonanuclear bismuth-oxo cations $[Bi_9(\mu_3\text{-}O)_8(\mu_3\text{-}OR)_6]^{5+}$ (R = H, Et)[25d] show a remarkable structural relationship with compound **3**. The cations might be described to be composed of a $[Bi_5O_6(OR)_6]$ subunit of type **E** and two edge-sharing trigonal $[Bi_3(\mu_3\text{-}O)]$ subunits.

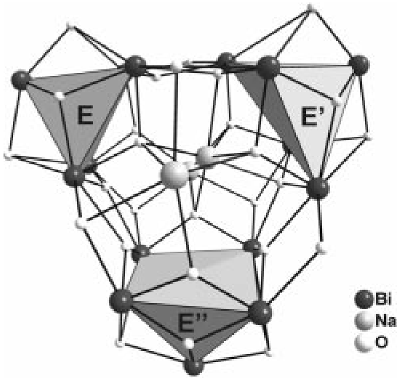

Figure 7. View of the $[Bi_{15}Na_3O_{30}]$ core structure of **3** (Me_3Si groups are omitted). Three sodium atoms connect the subunits **E**, **E′** and **E′′**.

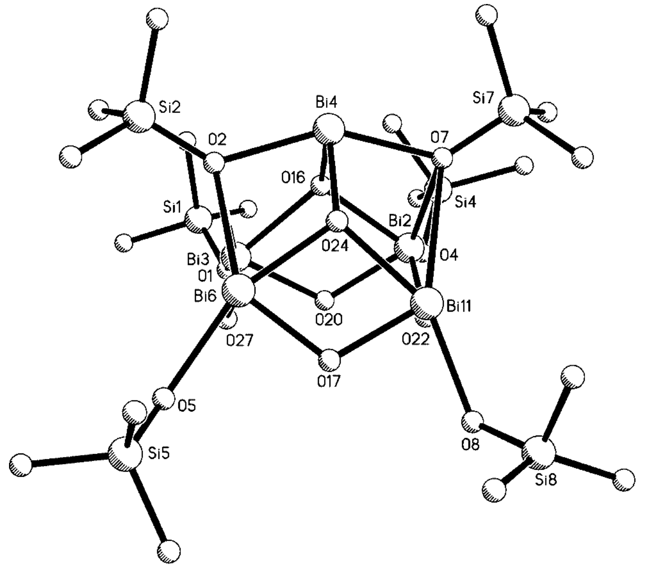

Figure 8. View of the $[Bi_5O_{12}]$ subunit **E** including Me_3Si groups. Two additional Bi–O bonds of Bi(2) and Bi(3) to O(29) and O(15), which are part of **E**′ and **E**″, are omitted. Selected bond lengths [Å] and angles [°]: Bi(3)–O(1) 2.532(11), Bi(3)–O(2) 3.196(11), Bi(3)–O(16) 2.310(9), Bi(3)–O(20) 2.066(9), Bi(3)–O(27) 2.254(10), Bi(4)–O(2) 2.260(9), Bi(4)–O(7) 2.243(9), Bi(4)–O(16) 2.033(9), Bi(4)–O(24) 2.079(9), Bi(6)–O(2) 2.737(9), Bi(6)–O(5) 2.378(9), Bi(6)–O(17) 2.084(10), Bi(6)–O(24) 2.214(9), Bi(6)–O(27) 2.115(8); Bi(4)–O(2)–Bi(3) 89.7(3), Bi(4)–O(2)–Bi(6) 96.0(3), Bi(3)–O(2)–Bi(6) 83.7(3), Bi(3)–O(16)–Bi(4) 127.8(4), Bi(3)–O(27)–Bi(6) 130.6(4), Bi(4)–O(24)–Bi(6) 120.5(4), O(2)–Bi(6)–O(5) 128.8(3), O(2)–Bi(6)–O(17) 135.6(3), O(2)–Bi(6)–O(24) 65.7(3), O(2)–Bi(6)–O(27) 76.7(3), O(5)–Bi(6)–O(17) 87.3(3), O(5)–Bi(6)–O(24) 158.4(4), O(5)–Bi(6)–O(27) 74.6(3), O(17)–Bi(6)–O(24) 73.2(4), O(17)–Bi(6)–O(27) 93.0(4), O(24)–Bi(6)–O(27) 96.8(4).

In addition, the metal-oxo core of the $[Bi_5O_{12}]$ subunit **E** shows some structural relationship to the $[Bi_3Na_2O_{13}]$ subunit **A** (Figure 4). The basic structural motif of both **A** and **E** is a square pyramid with the metal atoms occupying the corners (Figure 8). An additional oxygen atom in **A** occupies a position within the oxo cage. However, both subunits **E** and **A** can be deduced from the metal-oxo core of bismuth-oxo-hydroxo complexes[23] of the type $[Bi_6O_{4+x}(OH)_{4-x}]^{[6-x]+}$ by removal of one bismuth atom (Figure 4). It might be assumed that only in octahedral structures of the type $[Bi_xNa_yO_z]$ ($x + y = 6$) and $[Bi_xNa_y\square O_z]$ ($x + y = 5$, $\square$ = metal vacancy) with at least two sodium atoms the octahedral void might be occupied by an oxygen atom. Noteworthy, the additional oxygen atom in **A** results in a smaller instead of the expected larger volume of subunit **A** compared with that of **E**. This is best demonstrated by the metal–metal distances along the edges of the pyramid. In structure fragment **A** these distances are in the range 3.290(2)–3.460(2) Å whereas those in fragment **E** are in the range 3.430(1)–3.958(1) Å. In subunit **E** the Bi–O distances are in a large range between 2.033(9) Å and 3.196(12) Å, which is attributed to the combination of strong primary bonds and weak secondary interactions. As a result large distortions of the coordination polyhedra are observed. For example, Bi(6) shows four Bi–O bond lengths in the range 2.084(10)–2.378(9) Å, a significantly longer Bi–O bond length of 2.737(9) Å and O–Bi(6)–O angles in the range 65.7(3)–158.4(4)° (Figure 8). The coordination geometry in the first-coordination shell might be described as distorted *pseudo*-trigonal bipyramid (BiO_4X) built from O(5), O(17), O(24), O(27) and a stereochemically active lone pair. An additional secondary Bi–O bond to O(2) completes the coordination sphere to give a [4+1] coordination. Similarly, all bismuth atoms in compound **3** show irregular coordination geometries which are best described as 4-, [4+1] and [4+2] coordination, respectively.

The metal-oxo silanolate $[Bi_2Na_4O(OSiMe_3)_8]$ (**1**) can be recrystallised from benzene or toluene, but attempts to recrystallise it from THF failed. Instead, the novel heterobimetallic compound $[Bi_{14}Na_8O_{18}(OSiMe_3)_{14}(thf)_4]\cdot C_6H_6$ (**4**$\cdot C_6H_6$) was obtained. Its molecular structure is shown in Figure 9.

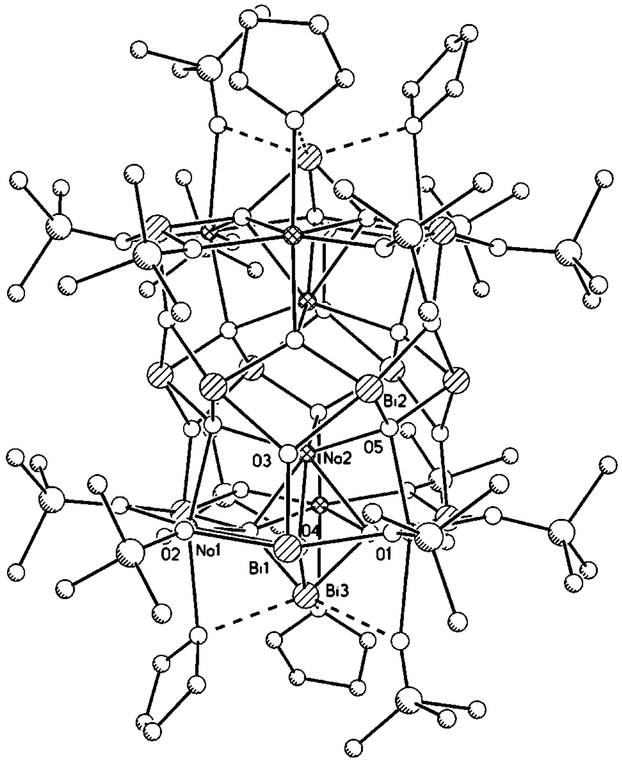

Figure 9. Molecular structure of $[Bi_{14}Na_8O_{18}(OSiMe_3)_{14}(thf)_4]$ (**4**); hydrogen atoms are omitted.

The molecular structure of compound **4** is best described to be composed of a symmetric $[(BiO_2)_6]^{6-}$ unit [Bi(2), O(3) and O(5)] which is sandwiched between two $[Bi_4Na_4O_3(OSiMe_3)_7(thf)_2]^{3+}$ subunits (Figure 10). The $[(BiO_2)_6]^{6-}$ unit resembles a small cylinder which is closed from both sides by Na(2) and Na(2D), respectively [Na(2)–Na(2D) 3.515(5) Å, Bi(2)–Bi(2A) 5.965(1) Å, Bi(2)–Bi(2D) 6.888(1) Å]. The bismuth atoms within the $[(BiO_2)_6]^{6-}$ ring show a *pseudo*-trigonal bipyramidal coordination geometry with Bi(2)–O distances of 2.103(3) Å and 2.268(3) Å. The *cis*-O–Bi–O angles amount to 74.70(9)° and 97.13(5)°, and the *trans*-O–Bi–O angle is 156.39(12)°. A similar cyclic structural arrangement of eight such [BiO_2] moieties was recently reported for the ethanol solvate of [$Bi(OEt)_3$]$_8$.[28] The subunit [$Bi_4Na_4O_3(OSiMe_3)_7(thf)_2$]$^{3+}$ is composed of a symmetric layer, which consists of three bismuth and three sodium atoms [Bi(1) and Na(1)], three μ_5-oxygen atoms [O(4)] and six μ_2-$OSiMe_3$ ligands [O(1) and O(2)]. The sodium atom Na(2) is placed above the layer and the bismuth atom Bi(3), two thf ligands as well as a silanolate ligand are placed below the layer. Within the layer the bond lengths between the metal atoms and the oxygen atoms of the silanolate ligands are found to be similar for sodium and bismuth with values in the range 2.270(3)–2.319(3) Å. In contrast Bi(1)–O(4) amounts to 2.057(3) Å and Na(1)–O(4) to 2.583(3) Å. The μ_5-oxygen atom O(4) is further coordinated to Na(1A), Na(2) [Na(2)–O(4) 2.540(3) Å] and Bi(3) [Bi(3)–O(4) 2.138(3) Å]. The coordination geometry of Bi(3) is best described as trigonal pyramidal [O(4)–Bi(3)–O(4A) 83.69(5)°]. Additionally, secondary bonds of Bi(3) to the three oxygen-donor ligands thf and $OSiMe_3$ are observed [Bi(3)–O(6) 2.776(5) Å]. A similar coordination of the bismuth atom was reported for [$Bi(OSiPh_3)_3(thf)_3$],[9] but in contrast to the terminal coordination of the thf ligands in the bismuth triphenylsilanolate those in compound **4** are bridging between Bi(3) and Na(1) [Na(1)–O(6) 2.513(4) Å].

The two subunits [$(BiO_2)_6$]$^{6-}$ and [$Bi_4Na_4O_3(OSiMe_3)_7(thf)_2$]$^{3+}$ are linked via O(3), O(5) and their symmetry related counterparts. Thus, μ_4-O(5) is connected to Na(1A), Na(2), Bi(2) and Bi(2B), and μ_3-O(3) to Bi(1), Bi(2) and Bi(2C) [O(5)–Na(1A)/Na(2)/Bi(2)/Bi(2B) 2.388(5)/2.446(3)/2.103(2)/2.103(2) Å; O(3)–Bi(1)/Bi(2)/Bi(2C) 2.045(3)/2.268(3)/2.268(3) Å]. The coordination geometry of Bi(1) is best described as *pseudo*-trigonal bipyramidal assigned to BiO_4X (X = lone pair). The *cis*-O–Bi–O angles are in the range 80.91(11)–91.66(10)° and the *trans*-O–Bi–O angle amounts to 161.65(11)°. Two short bonds between the bismuth atom and the *cis*-positioned oxygen atoms O(3) and O(4) [Bi(1)–O(3) 2.045(3) Å, Bi(1)–O(4) 2.057(3) Å] as well as two elongated bonds to the *trans*-located oxygen atoms O(1) and O(2) [Bi(1)–O(1) 2.319(3) Å, Bi(1)–O(2) 2.295(3) Å] are observed. Noteworthy, the sodium-rich bismuth-oxo cluster **4** is neither composed of the above-mentioned [M_5O_{12}] subunits nor of ladder type arrangements of type **C**. The structural relationship is restricted to the formation of trinuclear [Bi_3O] subunits, planar four-membered [Bi_2O_2] and [$NaBiO_2$] rings and strongly distorted bismuth-oxygen polyhedra.

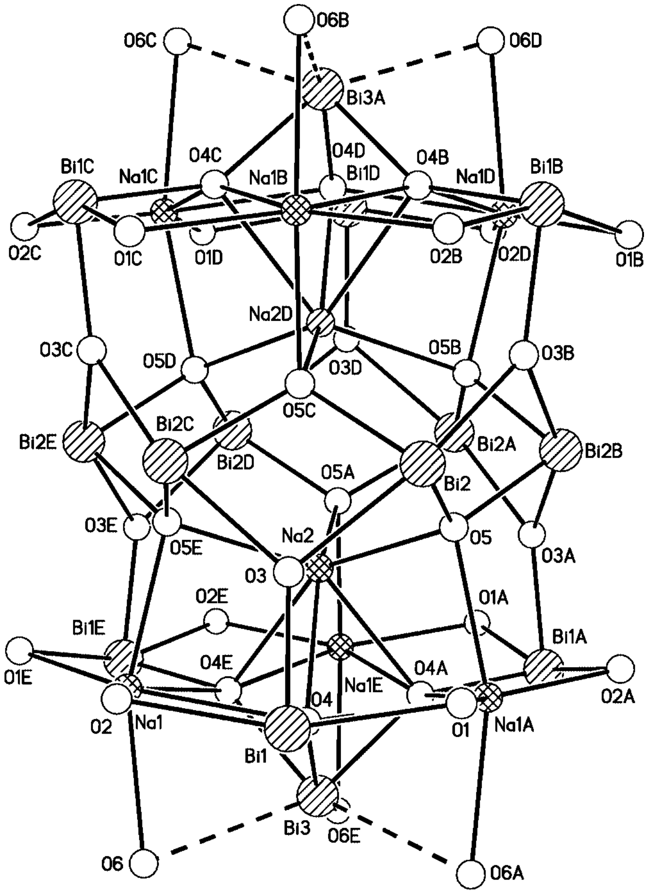

Figure 10. View of the metal-oxo core structure of **4** (Me_3Si groups, C and H atoms are omitted) showing the atom numbering scheme. Selected bond lengths [Å] and angles [°]: Bi(1)–O(1) 2.319(3), Bi(1)–O(2) 2.295(3), Bi(1)–O(3) 2.045(3), Bi(1)–O(4) 2.057(3), Bi(2)–O(3) 2.268(3), Bi(2)–O(3B) 2.263(3), Bi(2)–O(5) 2.103(2), Bi(2)–O(5C) 2.097(3), Bi(3)–O(4) 2.138(3), Bi(3)–O(6) 2.776(5), Na(1)–O(2) 2.270(3), Na(1)–O(1E) 2.277(3), Na(1)–O(5E) 2.388(3), Na(1)–O(6) 2.513(4), Na(1)–O(4) 2.583(3), Na(1)–O(4E) 2.535(3), Na(2)–O(5) 2.446(3), Na(2)–O(4) 2.540(3); O(1)–Bi(1)–O(2) 161.7(1), O(1)–Bi(1)–O(3) 81.0(1), O(1)–Bi(1)–O(4) 91.7(1), O(2)–Bi(1)–O(3) 80.9(1), O(2)–Bi(1)–O(4) 91.6(1), O(3)–Bi(1)–O(4) 90.6(1), O(5C)–Bi(2)–O(5) 94.3(1), O(5C)–Bi(2)–O(3B) 89.5(1), O(5)–Bi(2)–O(3B) 74.7(1), O(5C)–Bi(2)–O(3) 74.7(1), O(3)–Bi(2)–O(5) 88.9(1), O(3)–Bi(2)–O(3B) 156.4(1), O–Na(1)–O 67.6(1)–160.1(1), O–Na(2)–O 68.2(1)–148.2(1), Bi(1)–O(3)–Bi(2) 129.1(1), Bi(2)–O(5)–Bi(2B) 110.2(1), Bi(2)–O(3)–Bi(2C) 99.0(1). Symmetry operations used to generate equivalent atoms: A = $-x + y + 1, -x, z$; B = $y + 2/3, -x + y + 1/3, -z + 1/3$; C = $x - y - 1/3, x - 2/3; -z + 1/3$; D = $- x + 2/3; -y - 2/3; -z + 1/3$; E = $x - y - 1; x - 1, -z$.

Studies on the thermal behaviour of compounds **1**–**3** were carried out. The thermal stability of the clusters **2** and **3** is rather low as was shown by DTA-TG measurements. The onset of decomposition starts below 120 °C and is attributed to the loss of solvate molecules. The major weight loss for compounds **1**–**3** is observed between 150 °C and 250 °C. The observed weight loss (**1** 39.8%; **2** 27.6%; **3** 18.8%) is lower than calculated for the formation of pure Na/Bi/O phases and indicates formation of silicates. The observed values correspond to mixtures with general formulas such as $Bi_2Na_4Si_{2.5}O_{10}$ (calcd. 40.3%, **1b**), $Bi_{10}Na_5Si_{2.5}O_{10}$ (calcd. 26.6%, **2b**) and $Bi_{15}Na_4Si_3O_{30}$ (calcd. 19.0%, **3b**). It should be noted that the sillenite-type bismuth silicate $Bi_{12}SiO_{20}$ was observed upon thermal decomposition of [$Bi_{22}O_{16}(OSiMe_2tBu)_{22}$].[10] Similarly, the powder X-ray data of the decomposition products **2b** and **3b** were also indicative of $Bi_{12}SiO_{20}$ (JCPDS No. 76–726) as major crystalline material. In case of compound **2** Na_2SiO_3 (JCPDS No. 82–0604) was observed as an additional minor product. The latter was the only crystalline material in the mainly amorphous decomposition product **1b**.

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Conclusions

Both partial hydrolysis and elimination of $Me_3SiOSiMe_3$ from $[Bi(OSiMe_3)_3]$ contribute to the formation of heterobimetallic bismuth-oxo silanolates. We assume that $[Bi(OSiMe_3)_3]$ is formed in situ by reaction of $BiCl_3$ with $NaOSiMe_3$, but the reaction of the bismuth silanolate with additional $NaOSiMe_3$ to give $Me_3SiOSiMe_3$ is faster than the metathesis reaction. The favoured product is $[Bi_2Na_4O(OSiMe_3)_8]$ (**1**). Several different heterobimetallic byproducts are observed, the amounts of which depend on subtle changes in the reaction conditions. The use of THF as solvent favours the elimination of $Me_3SiOSiMe_3$, but its formation is also observed in non-polar solvents. It is noteworthy that in contrast to $[Bi(OSiMe_3)_3]$, the corresponding alkoxide $[Bi(OtBu)_3]$ is accessible via salt elimination. Despite of the ready M–O–M bond formation by elimination of $Me_3SiOSiMe_3$, thermolysis of heterometallic bismuth-oxo silanolates in the solid state results in silicate materials instead of heterobimetallic oxides. The Bi–$OSiMe_3$ moiety is very sensitive towards hydrolysis, and trace amounts of water induce hydrolysis/condensation processes to take place until the reactivity of the metal-oxo silanolate is significantly reduced. The resulting heterobimetallic compounds are covered by Me_3SiO ligands which are still moisture-sensitive but prevent further aggregation.

The peculiarity of sodium and bismuth to assemble into diverse heterobimetallic complexes is explained by their similar ionic radii, and their rich and variable coordination chemistry. As a consequence, heterobimetallic metal-oxo subunits such as the ladder-type $[Bi_{3-x}Na_xO_y]$ and square pyramidal $[Bi_{5-x}Na_xO_y]$ fragments constitute basic building blocks. Thermolysis of bismuth-oxo silanolates gives compounds of the Sillenite-type family, which are extensively studied because of their interesting optical properties such as photorefractivity and photoconductivity.[29] It might be anticipated that novel heterometallic bismuth compounds are accessible starting from heterobimetallic bismuth-oxo silanolate derivatives. Such bismuth-rich metal-oxo silanolates might serve as molecular precursors for doped materials of the Sillenite-type family.

Experimental Section

General Remarks: All manipulations were performed with exclusion of oxygen and moisture by using Schlenk-type techniques and argon atmosphere. Solvents were distilled from appropriate drying agents prior to use. Elemental analyses were performed on a LECO-CHNS-932 analyser. No satisfactory elemental analyses were obtained for compound **1** which is assigned to partial substitution of $OSiMe_3$ by O*t*Bu – isostructural $[Bi_2Na_4O(OtBu)_8]$ was reported previously[18] – and for compound **2** which is assigned to its high moisture sensitivity. The DTA-TG measurements were performed at a heating rate of 6 °C min^{-1} to a maximum temperature of 700 °C in an atmosphere of flowing argon using Al_2O_3 as reference material. The residues were examined by powder X-ray diffraction using a Phillips PW1050/25 diffractometer. ^1H and ^{29}Si NMR spectra were recorded at 400.13 MHz and 59.6 MHz, respectively. Chemical shifts (δ values given in ppm) were referenced against Me_4Si. The IR spectra were run as Nujol mulls and absorption bands assigned to the compounds in the range 400–1400 cm^{-1} are listed. Celite® (FLUKA) and sodium silanolate (Aldrich) were dried in vacuo at 120 °C prior to use. Bismuth trichloride (Lancaster) was heated at reflux in thionyl chloride, washed with pentane and dried in vacuo. $[Bi(OtBu)_3]$[5] and Me_3SiOH[30] were prepared according to literature procedures.

Synthesis of $[Bi_2Na_4O(OSiMe_3)_8]$ (1) (Method a): To a solution of $NaOSiMe_3$ (12.70 g, 113.2 mmol) in toluene (100 mL) was added anhydrous $BiCl_3$ (7.00 g, 22.2 mmol) in small portions at room temperature. The beige suspension was stirred at room temperature for one hour and heated at reflux for two hours. The solid material was filtered off through Celite® and the clear solution was concentrated to approximately 50 mL. Crystallisation at 4 °C gave colourless crystals of compound **1**. The first crop of crystals isolated was not analytically pure and an EDX analysis revealed the presence of chloride in addition to bismuth, sodium and silicon. The second crop of crystals (1.20 g, 9%) was analytically pure **1**, which decomposes upon heating above 150 °C. A small quantity of compound **1** was suspended in THF/benzene and after stirring overnight a clear yellow solution was obtained. From this solution moisture-sensitive single crystals of $[Bi_{14}Na_8O_{18}(OSiMe_3)_{14}(thf)_4]\cdot C_6H_6$ (**4**$\cdot C_6H_6$) were obtained and dried in vacuo.

Synthesis of 1 (Method b): A solution of Me_3SiOH (1.64 g, 18.2 mmol) in toluene (10 mL) was added dropwise to a solution of $[Bi(OtBu)_3]$ (2.61 g, 6.1 mmol) in toluene. All volatile components were removed in vacuo and the residue was dissolved in toluene. To this solution $NaOSiMe_3$ (1.36 g, 12.1 mmol) was added portionwise and the resulting suspension was heated at reflux for 1.5 h. The solid material was isolated by filtration and dried in vacuo to give compound **1** (2.86 g, 76%).

1: $C_{24}H_{72}Bi_2Na_4O_9Si_8$ (1239.4): C 23.3, H 5.9; found C 24.0, H 6.4. IR (Nujol) $\tilde{\nu}$ = 1298 w, 1258 m, 1246 m, 1021 m, 996 w, 980 w, 967 w, 925 m, 894 s, 829 s, 742 m, 724 sh, 675 w, 660 w, 620 vw, 584 w, 537 w, 462 w, 414 cm^{-1} w.

4: $C_{42}H_{126}Bi_{14}Na_8O_{32}Si_{14}$ (4646.3): C 10.9, H 2.7; found C 11.4, H 2.9. IR (Nujol) $\tilde{\nu}$ = 1257 m, 1241 m, 1051 w, 941 m, 910 m, 826 m, 740 m, 725 m, 668 w, 593 cm^{-1} m.

Synthesis of $[Bi_{10}Na_5O_7(OH)_6(OSiMe_3)_{15}]$ (2) and $[Bi_{15}Na_3O_{18}(OSiMe_3)_{12}]$ (3): To a solution of $BiCl_3$ (11.88 g, 37.4 mmol) in THF (180 mL) was added $NaOSiMe_3$ (12.70 g, 113.2 mmol) in small portions at room temperature to give a beige suspension. The solvent was evaporated, the residue extracted with hot toluene (150 mL) and the solid material filtered through Celite®. Evaporation of the solvent gave a solid containing Na, Bi and Si according to an EDX analysis. The residue was dissolved in toluene and the solution stored at 4 °C for several weeks. Single crystals of **2** were isolated by filtration and dried in vacuo to give 410 mg **2**. The filtrate was collected, the amount of the solvent was reduced to approximately 20 mL, and the solution was kept at 4 °C for several months to give single crystals of **3**. The colourless crystals were isolated by filtration and the solvent was removed from the crystals in vacuo to give 550 mg of **3**. Both compounds show a poor solubility, are moisture sensitive and decompose upon heating above 120 °C.

2: $C_{45}H_{141}Bi_{10}Na_5O_{28}Si_{15}$ (3756.6): C 14.4, H 3.8; found: C 13.4, H 3.0. IR (Nujol) $\tilde{\nu}$ = 3450 br, 1257 m, 1244 m, 1021 w, 925 s, 830 s, 741 m, 669 w, 632 w, 584 w, 536 w, 501 w, 410 cm^{-1} br.

3: $C_{43}H_{116}Bi_{15}Na_3O_{30}Si_{12}$ (4654.1): C 11.1, H 2.5; found: C 10.9, H 2.5. IR (Nujol) $\tilde{\nu}$ = 1258 m, 1244 m, 934 s, 921 s, 907 s, 828 s, 742 m, 674 w, 652 w, 632 m, 600 s, 543 w, 496 m, 442 w, 414 cm^{-1} w.

Table 1. Crystallographic data for $[Bi_2Na_4(O)(OSiMe_3)_8]$ (**1**), $[Bi_{10}Na_5O_7(OH)_6(OSiMe_3)_{15}]{\cdot}1.5C_7H_8$ (**2**$\cdot 1.5C_7H_8$), $[Bi_{15}Na_3O_{18}(OSiMe_3)_{12}]{\cdot}C_7H_8$ (**3**$\cdot C_7H_8$) and $[Bi_{14}Na_8O_{18}(OSiMe_3)_{14}(thf)_4]$ (**4**$\cdot C_6H_6$).

Compound	**1**	**2**$\cdot 1.5C_7H_8$	**3**$\cdot C_7H_8$	**4**$\cdot C_6H_6$
Empirical formula	$C_{24}H_{72}Bi_2Na_4O_9Si_8$	$C_{45}H_{141}Bi_{10}Na_5O_{28}Si_{15}\cdot 1.5C_7H_8$	$C_{36}H_{108}Bi_{15}Na_3O_{30}Si_{12}\cdot C_7H_8$	$C_{42}H_{126}Bi_{14}Na_8O_{32}Si_{14}\cdot 4thf\cdot C_6H_6$
Formula weight	1239.46	3894.88	4654.11	5012.85
Crystal system	trigonal	triclinic	monoclinic	trigonal
Space group	$R\bar{3}c$	$P\bar{1}$	$C2/c$	$R\bar{3}$
Cell constants [Å, °]	$a = 12.8844(3)$	$a = 15.0377(2)$	$a = 54.311(11)$	$a = 15.9786(4)$
		$b = 16.0373(2)$	$b = 19.846(4)$	
	$c = 54.6565(3)$	$c = 27.8967(5)$	$c = 22.885(5)$	$c = 46.8329(17)$
		$\alpha = 87.1321(6)$		
		$\beta = 86.6530(7)$	$\beta = 112.32(3)$	
		$\gamma = 63.6617(6)$		
Volume [Å^3]	7857.8(3)	6016.8(2)	22819(8)	10355.2(5)
Z	6	2	8	3
$d_{calcd.}$ [g·cm^{-3}]	1.572	2.150	2.709	2.412
Absorption coefficient [mm^{-1}]	6.961	14.788	23.230	17.976
Crystal size [mm]	0.23 × 0.15 × 0.10	0.15 × 0.15 × 0.05	0.15 × 0.08 × 0.03	0.20 × 0.18 × 0.05
θ range for data collection [°]	3.16 to 27.46	2.93 to 27.52	2.94 to 25.41	2.98 to 27.49
No. of reflections collected	16688	70719	174201	62724
No. of unique reflections	2006 [$R_{int} = 0.039$]	27464 [$R_{int} = 0.059$]	20955 [$R_{int} = 0.133$]	5276 [$R_{int} = 0.073$]
R [$I > 2\sigma(I)$]	0.0285	0.0371	0.0445	0.0217
wR_2 (all data)	0.0381	0.0627	0.0809	0.0386
Largest diff. peak/hole [e·Å^{-3}]	0.318/–0.479	1.559/–1.526	3.240/–1.579	1.832/–1.956

Structure Determination: See Table 1. Intensity data for the colourless crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo-$K\alpha$ radiation at 173 K. The data collection covered almost the whole sphere of reciprocal space with two (**1**), four (**2**$\cdot 1.5C_7H_8$) and seven sets (**3**$\cdot C_7H_8$, **4**$\cdot C_6H_6$) at different κ-angles and 202 (**1**), 510 (**2**$\cdot 1.5C_7H_8$), 652 (**3**$\cdot C_7H_8$) and 592 (**4**$\cdot C_6H_6$) frames via ω-rotation ($\Delta/\omega = 1°$) at two times 30 s (**1**), 60 s (**2**$\cdot 1.5C_7H_8$), 157 s (**3**$\cdot C_7H_8$) and 60 s (**4**$\cdot C_6H_6$) per frame. The crystal–detector distance was 3.4 cm (**1**, **4**$\cdot C_6H_6$), 4.4 cm (**2**) and 3.8 cm (**3**$\cdot C_7H_8$). Crystal decay was monitored by repeating the initial frames at the end of data collection. Analysing the duplicate reflections there was no indication for any decay. The structures were solved by direct methods SHELXS97[31] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97.[32] The H atoms were placed in geometrically calculated positions using a riding model with U_{iso} constrained at 1.2 times U_{eq} of the carrier C atom for non-methyl and 1.5 times U_{eq} of the carrier C atom for methyl groups. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from the *International Tables for X-ray Crystallography.* Absorption correction was carried out with multi-scan using SCALEPACK[33] [$T_{min} = 0.310$, $T_{max} = 0.543$ (**1**); $T_{min} = 0.245$, $T_{max} = 0.525$ (**2**$\cdot 1.5C_7H_8$); $T_{min} = 0.085$, $T_{max} = 0.543$ (**3**$\cdot C_7H_8$); $T_{min} = 0.119$, $T_{max} = 0.467$ (**4**$\cdot C_6H_6$)]. In **1** disorder of the metal atoms was found. Bi1 and Na1 were refined with equal position and occupancies of 0.33 and 0.66, respectively. In **2**$\cdot 1.5C_7H_8$ disorder over two positions was found for C6C, C6C′, C8A, C8A′, C8B, C8B′ with occupancies of 0.5. All solvent molecules toluene (C51–C57, C61–C67) and disordered atoms were refined isotropically. One solvent molecule toluene (C61–C67) was refined with occupancies of 0.5. In **3**$\cdot C_7H_8$ disorder over two positions was found for C5A–C5′, C6A–C6′, C8A, C8′, C8B, C8′′, C9A–C9′, C10A–C10′, C11A–C11′ with occupancies of 0.5, for C12A, C12B with occupancies of 0.7 and for C12′, C12′′ with occupancies of 0.3. All solvent molecules toluene (C21–C27, C31–C37) and disordered atoms were refined isotropically. The solvent molecules toluene were refined with occupancies of 0.5. In **4**$\cdot C_6H_6$ a trimethylsilanolate ligand and a solvent molecule THF share the oxygen atom O6. The $SiMe_3$ group (Si3, C11–C13) was refined with occupancies of 0.33 and the C atoms of the solvent molecule THF (C7–C10) were refined with occupancies of 0.66. Si3, C7–C10 were refined anisotropically and C11–C13 were refined isotropically. The figures were created by SHELXTL[34] and DIAMOND (release 2.1e, 2001).

CCDC-276495 (for **1**), -276497 (for **2**$\cdot 1.5C_7H_8$), -276496 (for **3**$\cdot C_7H_8$) and -276498 (for **4**$\cdot C_6H_6$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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