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Polyhedral antimony(III) and bismuth(III) siloxanes: Synthesis, spectral studies, and structural characterization of $[Sb(O_3SiR)]_4$ and $[Bi_{12}(O_3SiR)_8(\mu_3-O)_4Cl_4(THF)_8]$ (R = $(2,6-iPr_2C_6H_3)N(SiMe_3)$)

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Dedicated to Professor M.F. Lappert.

Abstract

The antimony(III) and bismuth(III) containing siloxanes $[Sb(O_3SiR)]_4$ (2) and $[Bi_{12}(O_3SiR)_8(\mu_3-O)_4Cl_4(THF)_8]$ (3) (R = (2,6*i*Pr₂C₆H₃)N(SiMe₃)) have been prepared by the reaction of lipophilic N-bonded silanetriol 1 with the corresponding metal amides M(NMe₂)₃ (M = Sb, Bi). The composition and molecular structures of 2 and 3 have been fully determined by mass spectrometry, IR, NMR spectroscopy, elemental analysis, and lower temperature X-ray crystal structural analyses. Compound 2 represents the first example of a structurally characterized cubic antimony(III) containing siloxane ligands, whereas compound 3 exhibits a new highly soluble bismuth(III) cluster containing chloride and siloxane ligands. Hydrophobic groups, surrounding the central Si₄O₁₂Sb₄ and Bi₁₂Cl₄O₂₈Si₈ cores, play an important role in the high solubility of compounds 2 and 3 in common organic solvents. Several attempts to assemble the analogous bismuth(III) containing chloride free siloxane cluster were not successful. In our hands only the chlorine containing cluster resulted in the formation of single crystals.

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1. Introduction

There has been recently great interest in the synthesis and characterization of metallasiloxanes containing the Si–O–M motif (M = main group or transition metal) [1– 3], although the first reports date back to the end of the 19th century [4]. The soluble metallasiloxanes derived from –SiOH groups indeed act as structural model compounds for the heterogeneous metal incorporated zeolites [5]. The core structures of the Group 13 [6] and titanium [7] containing cubic metallasiloxanes act as the secondary building blocks (SBU) of Group 13 and titanium containing zeolites. Furthermore, these compounds are quite valuable in understanding the reaction path and the intermediate steps formed during the catalytic processes, particularly those involving silica supported transition metal catalysts [8]. We have, for example, shown that cubic titanasiloxanes [RSiO₃Ti R_1]₄ [R = (2,6-*i*Pr₂C₆H₃)N(SiMe₃)] [R_1 = Et, *i*Pr] apart from being good models for titanium containing zeolites such as TS-1 and TS-2, are also good catalysts, especially for epoxidation of cyclo-hexene and cyclo-octene [9]. Moreover, the metallasiloxanes can also be considered as precursors for silicon polymers containing metal centers in the polymeric backbone [10].

In view of the importance of such compounds, we have been actively involved in the synthesis of metallasiloxanes starting from lipophilic N-bonded silanetriol $RSi(OH)_3$ ($R = (2,6-iPr_2C_6H_3)N(SiMe_3)$) (1) with metal alkyls, metal

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alcoholates, and metal amides as the precursor under the elimination of alkanes, alcohols, and amines, respectively [1a-i]. Among them, compounds with a cubic core structure are of particular interest [6,7,11]. In this direction, we synthesized a range of Al-, Ge-, In-, Ge-, Sn- Ti-, Fe-, and Zn-containing siloxanes with cubic M₄O₁₂Si₄ frameworks. With this in mind, it was of interest to extend our studies towards the preparation of soluble analogous molecular antimony(III), and bismuth(III) containing siloxane frameworks. Previously, Schmidbaur [12a,12b] and Hubert-Pfalzgraf et al. [13a] have reported on antimony(III), and bismuth(III) containing siloxane compounds which were obtained by use of R₃SiO. Feher et al. synthesized cubic Group 15 containing heterosilsesquioxanes by the "corner-capping" reaction starting from three-functional, incompletely condensed oligosilsesquioxanes (c-C₆H₁₁)₇Si₇O₉(OH)₃ [14a], those structures could not be completely solved except the phosphorus congener. However, these compounds have a metal/silicon ratio of 1:7 [14]. Recently, Mehring et al. reported on a polyhedral bismuth siloxane of composition [Bi22O26(OSi- Me_2tBu_{14}] [13d,13e].

In this paper, we present the synthesis, spectral studies, and structural characterization of the $[Sb(O_3SiR)]_4$ (2) and $[Bi_{12}(O_3SiR)_8(\mu_3-O)_4Cl_4(THF)_8]$ (3) (R = $(2,6-iPr_2C_6H_3)N-$ (SiMe₃)). These compounds have the Sb/Si and Bi/Si ratios of 4:4 and 12:8, respectively. Compound 2 represents the first example of fully characterized cubic antimony(III) containing siloxane ligands. More recently, the antimony silicate (Sb/Si molar ratio of 1:1) has been found to be useful as a high selective ion exchanger for the removal of ⁸⁵Sr from nuclear waste solutions [15], whereas bismuth silicate, as an anion exchanger [16], has been used as a novel sorbent in thin layer chromatography [17]. Furthermore, antimony and bismuth silicate glasses find a number of industrial and special applications such as, fiber optic amplifiers [18], high temperature superconductors, and capacitor layers in memory devices [19].

2. Results and discussion

2.1. Synthesis and spectroscopic characterization of compound 2

The reaction of (arylamino) silanetriol [20] $RSi(OH)_3$ (R = (2,6-*i*Pr₂C₆H₃)N(SiMe₃)) (1) with antimony(III) amide [21] Sb(NMe₂)₃ in hexane and THF at room temperature with a 1:1 stoichiometric ratio afforded the cuboid antimony(III) siloxane [Sb(O₃SiR)]₄ (R = (2,6-*i*Pr₂C₆H₃)-N(SiMe₃)) (2) in about 83% yield (Scheme 1).

The reaction proceeds under evolution of dimethylamine HNMe₂, which results in the subsequent assembly of the three-dimensional Si-O-Sb frameworks. Compound 2 is highly soluble in common organic solvents such as hexane, benzene, toluene, ether or THF. Compound 2 has been fully characterized by means of analytical, spectroscopic, and single-crystal X-ray diffraction studies. An interesting aspect of the antimony(III) siloxane 2 is that, in spite of the large molecular weight, the electron impact mass spectrum (EIMS) of compound 2 reveals a strong parent molecular ion in the range of m/z 1781–1792 $([M^+] 1784.2$ relative intensity: 100%) that possesses an isotopic cluster pattern that is also consistent with the expected composition as shown in Fig. 1. This observation indicates that, under ionization conditions (70 eV), the cubic core of compound 2 remains intact. Besides this, compound 2 does not melt up to 387°C, at which point the color of the compound turns into black brown. The IR spectrum of compound 2 shows an absorption between 900 and 1000 cm^{-1} , which could be attributed to Si–O–Sb



Scheme 1. Synthesis of compounds 2 and 3.



Fig. 1. (a) A partial mass spectrum (electron impact) of **2** showing the parent ion in the m/z 1781 to 1792 range. (b) A simulated isotope cluster pattern expected for the C₆₀H₁₀₄N₄O₁₂Sb₄Si₈ composition.

stretching frequency. The ¹H NMR spectral data (in C_6D_6) and the integration of the intensities match well with the proposed structure of compound 2. The protons from the -SiMe₃ groups resonate as a singlet ($\delta = 0.25$ ppm). Two sets of doublets of equal intensity appear at $\delta = 1.23$ and 1.26 ppm (J = 6.9 Hz) for the two isopropyl methyl (CH(CH₃)₂) protons, while a septet ($\delta = 3.75$ ppm, J = 6.9 Hz) is observed for the isopropyl methine $(CH(CH_3)_2)$ proton. The appearance of two different resonances for isopropyl groups is consistent with the crystal structure of 2 if the rotation of the aromatic groups about the C-N bond is restricted. The aryl protons of compound **2** resonate as a multiplet in the range of $\delta = 6.66-6.69$ ppm. The ²⁹Si NMR spectrum of compound 2 (in C₆D₆) displays two single resonances for the Me₃SiN unit ($\delta = 4.4$ ppm) and for the O₃SiN part ($\delta = -91$ ppm), indicating a high symmetry in solution.

2.2. Structural description of 2

Unequivocal proof of the structure for compound 2 has been provided by the crystallographic analysis of single crystals. Single crystals of 2 suitable for X-ray structural determination were grown from their concentrated hexane/THF solution. Compound 2 crystallizes in the monoclinic space group $P2_1/n$, along with two independent molecules and 2.68 molecules of THF in the asymmetric unit. The structure refinement data of compounds 2 and 3 are listed in Table 1. Selected metric parameters of 2 are summarized in Table 2. The ORTEP core structure diagrams of both independent molecules of 2 are shown in Fig. 2. The Si₄O₁₂Sb₄ core structure can be defined by four silicon and four antimony atoms occupying alternate corners of the distorted cubic polyhedron. Each of the 12 Si...Sb edges is bridged by oxygen atoms in a μ -bridging fashion. There are six Si₂O₄Sb₂ eight-membered rings that define the faces of the cube, and each of these rings adopts a pseudo C_4 crown conformation.

It is interesting to note that none of the antimony atoms have any other ligands in their coordination environment except oxygen. The antimony atoms adopt distorted trigonal pyramidal geometry. The warped form of the trigonal pyramidal geometry may be attributed to the lone pair repulsions. The O–Sb–O angles are observed in the range from 91.1(1)° [O(4)–Sb(3)–O(7)] to 100.4(1)° [O(3)–Sb(1)– O(6)] with the average angle of 95.6°. This value compares well with the data reported for [Sb(OSiMe₃)₃] [12a] av. 95.2°. However, the silicon atom shows nearly ideal tetrahedral geometry. The O–Si–O angles are observed in the range from 108.0(2)° [O(20)–Si(13)–O(19)] to 112.8(2)° [O(10)–Si(1)–O(12)] with an average angle of 109.7°.

The Sb–O bond distances in **2** vary in the range of 1.914(3) Å [Sb(7)–O(17)] to 1.955(3) Å [Sb(5)–O(19)] with an average value of 1.940 Å. These are slightly longer than the corresponding ones found for [Sb(OSiMe₃)₃] [12a] (av. 1.935 Å). The Si–O bond distances are seen in the range of

Table 1 Crystal data and structure refinement for compounds **2** and **3**

	$2 \cdot 1.34 C_4 H_8 O$	$3 \cdot 2 C_4 H_8 O$
Formula	C _{65,37} H _{114,73} N ₄ O _{13,34} Sb ₄ Si ₈	C160H288Bi12Cl4N8O38Si16
Formula weight	1881.92	6030.98
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
$T(\mathbf{K})$	100(2)	133(2)
λ (Å)	1.54178	0.71073
<i>a</i> (Å)	27.075(6)	22.9236(7)
b (Å)	14.923(4)	19.0353(5)
<i>c</i> (Å)	41.644(10)	23.7193(8)
α (°)	90	90
β (°)	94.93(3)	94.025(3)
γ (°)	90	90
$V(\text{\AA}^3)$	16764(7)	10324.6(5)
Ζ	8	2
$\rho_{\rm calc} ({\rm g/cm}^3)$	1.491	1.940
$\mu (\mathrm{mm}^{-1})$	11.666	10.396
<i>F</i> (000)	7661	5792
θ Range for data collection (°)	1.02–29.52	1.28–24.36
Index ranges	$-26 \leq h \leq 30, -16 \leq k \leq 16, -41 \leq l \leq 43$	$-26 \leqslant h \leqslant 26, \ -22 \leqslant k \leqslant 21, \ -27 \leqslant l \leqslant 27$
Number of reflections collected	118007	54953
Number of independent reflections (R_{int})	23725 (0.0797)	16691 (0.0672)
Number of data/restraints/parameters	23725/2690/2075	16691/0/1025
Goodness-of-fit on F^2	1.003	1.021
R_1 , ^a wR_2^{b} ($I \ge 2\sigma(I)$)	0.0367, 0.0681	0.0329, 0.0681
R_1 , ^a wR_2 ^b (all data)	0.0627, 0.0764	0.0483, 0.0772
Largest difference peak/hole (e $Å^{-3}$)	0.742/-0.624	1.589/-1.196

^a
$$R = \sum ||F_0| - |F_c|| / \sum |F_0|.$$

^b $wR_2 = [\sum w(F_2^2 - F_2^2)^2 / \sum w(F_2^2)^2]^{1/2}.$

1.595(4) Å [Si(5)–O(7)] to 1.638(4) Å [Si(1)–O(2)] with an average value of 1.62(4) Å, similar to the reported data found in [RSiO₃Al · THF]₄ (R = $(2,6-iPr_2C_6H_3)N(SiMe_3)$) [6c]. The distortion of the cube is indicated by the broad range of the Sb–O–Si angles. Thus, the Sb–O–Si angles within the framework are in the range of 128.9(2)° [Si(5)–O(8)–Sb(4)] to 158.1(2)° 1 [Si(13)–O(20)–Sb(8)] (av. 142.5°).

2.3. Synthesis and spectroscopic characterization of compound **3**

Compound 3 is synthesized by the addition of a hexane solution of bismuth(III) amide [22] to a suspension of $RSi(OH)_3$ (R = (2,6-*i*Pr₂C₆H₃)N(SiMe₃)) (1) in 1:1 molar ratio, at room temperature, in about 23% yield (Scheme 1). The formation of 3 proceeds with the evolution of dimethylamine gas and a self-condensation of the silanetriol to generate the disiloxanetetrol $[(RSi(OH)_2)_2O]$ and water. This process is presumably catalyzed by bismuth(III) amide. Such a condensation reaction has been noted by us earlier in the presence of hydrazine [23]. Furthermore, during the course of the reaction, two molecules of dimethylamine are eliminated, resulting in the capping of the three Bi(III) centers by the oxygen of liberated water molecule. The yield of **3** highly depends on the chloride containing bismuth(III) amide. For the preparation of bismuth(III) amide [22] we followed the literature method. However, the bismuth(III) amide in our hands was more or less contaminated with chloride. Thus, the overall synthesis of $[Bi_{12}(O_3SiR)_8(\mu_3-O)_4Cl_4(THF)_8]$ (R = $(2,6-iPr_2C_6H_3)N-(SiMe_3)$) (3) involves, eight molecules of silanetriol, eight molecules of Bi(NMe₂)₃, four molecules of Bi(NMe₂)₂Cl, and four molecules of water under elimination of 32 molecules of HNMe₂.

Compound 3 has been characterized based on its analytical, spectroscopic, and mass spectrometric data. Interestingly, compound 3 does not melt up to 398 °C and decomposes without melting on further heating. However, no peak attributable to the molecular ion of 3 can be observed in the EI or other mass spectrometric methods. Only smaller fragment ion peaks are found. Similar to compound $[Bi_{22}O_{26}(OSiMe_2tBu)_{14}]$ [13d,13e], compound 3 is also good soluble in common hydrocarbon solvents, such as benzene. Like 2, 3 also shows the absence of a characteristic strong broad IR absorption centered around 3400 cm⁻¹, indicating that all of the Si–OH groups of 1 have reacted and the IR spectrum is dominated by the typical M-O-Si stretching frequencies observed in the range of 900- 1000 cm^{-1} . It is difficult to deduce the structure of compound **3** as its ¹H NMR spectrum (in C_6D_6) revealed several multiple resonances for the methyl (SiMe₃, and iPr), isopropyl – CH, aryl protons, and (slightly broad) coordinated THF molecule protons. Nevertheless, the ²⁹Si NMR spectrum of compound 3 (in C_6D_6) displays the presence of six resonances, out of which the first three are assigned for the

Table 2		
Selected bond lengths (Å) and	bond angles (°) for	compounds 2 and 3

Compound 2 · 1.34 THF					
Molecule 1					
Sb(1)–O(3)	1.954(3)	Sb(3)–O(11)	1.951(3)	Si(3)–O(5)	1.602(4)
Sb(1)–O(6)	1.952(4)	Sb(4) - O(8)	1.949(3)	Si(3) - O(6)	1.619(4)
Sb(1) = O(9)	1.951(3)	Sb(4) = O(12)	1.953(3)	Si(5) - O(7)	1.595(4)
Sb(2) = O(2)	1 943(3)	Sb(4) = O(1)	1 919(3)	Si(5) = O(8)	1 630(4)
Sb(2) - O(5)	1.945(3)	Si(1) = O(1)	1.603(4)	Si(5) - O(9)	1.625(4)
Sb(2) = O(3)	1.917(3)	$S_{1}(1) = O(1)$ $S_{2}(1) = O(2)$	1.605(4)	Si(3) = O(3) Si(7) = O(10)	1.023(4) 1.624(4)
SD(2) = O(10)	1.951(3)	SI(1) = O(2)	1.038(4)	SI(7) = O(10)	1.024(4)
Sb(3) = O(4)	1.945(3)	$S_1(1) = O(3)$	1.621(4)	$S_1(7) = O(11)$	1.629(4)
Sb(3) - O(7)	1.931(3)	$S_1(3) - O(4)$	1.632(4)	Si(7) - O(12)	1.616(4)
O(9)-Sb(1)-O(6)	98.4(1)	O(1)-Si(1)-O(3)	108.3(2)	Si(1)-O(1)-Sb(4)	157.3(2)
O(9)–Sb(1)–O(3)	99.3(1)	O(1)-Si(1)-O(2)	109.5(2)	Si(1) - O(2) - Sb(2)	129.1(2)
O(6)-Sb(1)-O(3)	100.4(1)	O(3) - Si(1) - O(2)	110.0(2)	Si(1) - O(3) - Sb(1)	143.2(2)
O(5)-Sb(2)-O(2)	92.3(1)	O(5)-Si(3)-O(6)	108.7(2)	Si(3)–O(4)–Sb(3)	129.2(2)
O(5)-Sb(2)-O(10)	93.7(1)	O(5)-Si(3)-O(4)	108.9(2)	Si(3) - O(5) - Sb(2)	156.7(2)
O(2)-Sb(2)-O(10)	96.7(1)	O(6) - Si(3) - O(4)	110.4(2)	Si(3) - O(6) - Sb(1)	141.3(2)
O(7) - Sb(3) - O(4)	91 1(1)	O(7) = Si(5) = O(9)	108 9(2)	Si(5) = O(7) = Sb(3)	1542(2)
O(7)-Sb(3)-O(11)	93 1(1)	O(7) - Si(5) - O(8)	109.3(2)	Si(5) = O(8) = Sb(4)	128.9(2)
O(4) = Sb(3) = O(11)	97.8(1)	O(9) = Si(5) = O(8)	109.5(2) 109.7(2)	Si(5) = O(9) = Sb(1)	120.9(2) 140.9(2)
O(1) Sb(3)- $O(11)$	97.0(1)	O(12) $S(7)$ $O(10)$	112 8(2)	Si(3) = O(3) = Si(1) Si(7) = O(10) = Sh(2)	140.9(2)
O(1) = Sb(4) = O(8)	92.1(1)	O(12) - S(7) - O(10)	112.0(2)	SI(7) = O(10) = SD(2) SI(7) = O(11) = SF(2)	142.5(2)
O(1) - SD(4) - O(12)	92.6(1)	O(12) - Si(7) - O(11)	109.7(2)	SI(7) = O(11) = SD(3)	141.4(2)
O(8) - Sb(4) - O(12)	98.0(1)	$O(10) - S_1(7) - O(11)$	110.8(2)	$S_1(7) = O(12) = Sb(4)$	142.0(2)
Molecule 2					
Sb(5) O(18)	1.047(2)	Sb(7) O(22)	1.046(2)	S(0) O(14)	1 624(4)
Sb(5) = O(18)	1.947(3)	Sb(7) = O(22) Sb(8) $O(15)$	1.940(3)	Si(9) = O(14) Si(0) = O(15)	1.034(4)
SD(3) = O(19)	1.955(3)	SD(8) = O(15)	1.943(3)	SI(9) = O(15)	1.028(4)
Sb(5) - O(23)	1.943(3)	Sb(8) - O(16)	1.950(3)	$S_1(11) - O(16)$	1.632(3)
Sb(6) - O(13)	1.944(3)	Sb(8)–O(20)	1.920(3)	Si(11) - O(17)	1.604(4)
Sb(6)–O(21)	1.949(3)	Si(15)–O(22)	1.632(3)	Si(11)–O(18)	1.629(4)
Sb(6)–O(24)	1.923(3)	Si(15)–O(23)	1.630(4)	Si(13)–O(19)	1.626(3)
Sb(7)–O(14)	1.949(3)	Si(15)–O(24)	1.600(3)	Si(13)-O(20)	1.602(3)
Sb(7)-O(17)	1.914(3)	Si(9)-O(13)	1.625(3)	Si(13)-O(21)	1.633(4)
O(22) $S1(5)$ $O(10)$	00.1(1)	O(12) $O'(0)$ $O(15)$	112 4(2)	S'(0) O(12) SI(()	142.8(2)
O(23) = SO(3) = O(18)	99.1(1)	O(13) = SI(9) = O(13)	112.4(2)	SI(9) = O(13) = SO(0)	142.6(2)
O(23) - SD(5) - O(19)	99.8(1)	O(13) - Si(9) - O(14)	110.5(2)	SI(9) = O(14) = SD(7)	141.9(2)
O(18) - Sb(5) - O(19)	99.9(1)	O(15) - Si(9) - O(14)	110.0(2)	$S_1(9) = O(15) = Sb(8)$	141.1(2)
O(24)-Sb(6)-O(13)	93.5(1)	O(17) - Si(11) - O(18)	108.8(2)	Si(11) - O(16) - Sb(8)	129.5(2)
O(24)-Sb(6)-O(21)	91.9(1)	O(17) - Si(11) - O(16)	109.3(2)	Si(11) - O(17) - Sb(7)	157.2(2)
O(13)–Sb(6)–O(21)	96.1(1)	O(18)–Si(11)–O(16)	110.0(2)	Si(11)–O(18)–Sb(5)	143.1(2)
O(17)–Sb(7)–O(22)	91.8(1)	O(20)-Si(13)-O(19)	108.0(2)	Si(13)–O(19)–Sb(5)	143.5(2)
O(17)-Sb(7)-O(14)	93.1(1)	O(20)-Si(13)-O(21)	109.6(2)	Si(13)–O(20)–Sb(8)	158.1(2)
O(22)-Sb(7)-O(14)	99.1(1)	O(19)-Si(13)-O(21)	110.1(2)	Si(13)–O(21)–Sb(6)	129.4(2)
O(20)-Sb(8)-O(15)	93.5(1)	O(24)-Si(15)-O(23)	108.2(2)	Si(15) - O(22) - Sb(7)	130.4(2)
O(20) = Sb(8) = O(16)	92.5(1)	O(24) = Si(15) = O(22)	108 7(2)	Si(15) = O(23) = Sb(5)	1414(2)
O(15)-Sb(8)-O(16)	97.3(1)	O(23)-Si(15)-O(22)	110.3(2)	Si(15) - O(24) - Sb(6)	155.6(2)
Compound 3					
$\frac{1}{\mathbf{P}'(1) \cdot \mathbf{Q}(1)}$	2.0(9(5)		O(1) D' (1) $O(12)$		00.0(2)
B1(1) = O(1)	2.068(5)		O(1) - Bi(1) - O(13)		89.8(2)
$B_1(1) - O(13)$	2.139(5)		O(1)-Bi(1)-O(7)		91.4(2)
Bi(1) - O(7)	2.272(5)		O(13) - Bi(1) - O(7)		71.74(18)
Bi(1)-O(4)	2.476(5)		O(1)-Bi(1)-O(4)		91.3(2)
Bi(1)-O(2L)	2.893(7)		O(13)-Bi(1)-O(4)		67.71(17)
Bi(2)–O(2)	2.067(6)		O(1)-Bi(1)-O(2L)		80.4(2)
Bi(2)–O(13)	2.149(5)		O(13)-Bi(1)-O(2L)		159.9(2)
Bi(2)-O(10)	2.245(5)		O(7) - Bi(1) - O(2L)		125.7(2)
Bi(2)–O(7)	2.451(5)		O(4) - Bi(1) - O(2L)		94.8(2)
Bi(3) - O(3)	2.086(5)		O(2) - Bi(2) - O(13)		89.5(2)
Bi(3) = O(13)	2 155(5)		O(2) - Bi(2) - O(10)		89 5(2)
Bi(3) - O(4)	2.105(0) 2.307(5)		O(13) = Bi(2) = O(10)		72 51(10)
$B_{i}(3) - O(10)$	2.507(5)		$O(2)_{R}(2) O(10)$		00.06(10)
$B_{i}(3) = O(10)$ $B_{i}(3) = O(15)$	2.312(0)		O(2) = D(2) = O(7) O(13) = D(2) = O(7)		20.20(19)
$\mathbf{D}_{1}(3) = O(13)$ $\mathbf{D}_{2}(4) = O(8)$	2.075(7)		O(13) - DI(2) - O(7) O(2) = D(2) - O(12)		00.00(18)
$\mathbf{DI}(4) = \mathbf{O}(\delta)$	2.084(5)		O(3) - BI(3) - O(13)		89.3(2)
B1(4) - O(5)	2.100(5)		O(3) - Bi(3) - O(4)		90.9(2)
B1(4)-O(14)	2.230(5)		O(13)-B1(3)-O(4)		70.74(18)
$B_1(4) - O(3L)$	2.794(5)		O(3)-Bi(3)-O(10)		89.99(18)

Table 2	(continued
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Compound 3			
Bi(5)-O(11)	2.115(5)	O(13)-Bi(3)-O(10)	67.21(17)
Bi(5)–O(6)	2.136(5)	O(3)-Bi(3)-O(15)	80.4(2)
Bi(5)-O(14)	2.151(5)	O(4)-Bi(3)-O(15)	98.8(2)
Bi(6)-O(12)	2.102(5)	O(8)-Bi(4)-O(5)	89.6(2)
Bi(6)–O(9)	2.144(5)	O(8)-Bi(4)-O(14)	89.61(18)
Bi(6)-O(14)	2.236(5)	O(5)-Bi(4)-O(14)	90.43(19)
Bi(6)–O(16)	2.698(6)	O(8)-Bi(4)-O(3L)	73.5(2)
Bi(5)-Cl(2)	2.851(2)	O(5)-Bi(4)-O(3L)	76.4(2)
Bi(5)-Cl(1)	2.966(2)	O(14)-Bi(4)-O(3L)	158.4(2)
Bi(6)-Cl(2)	2.885(2)	O(11)–Bi(5)–O(6)	86.2(2)
Bi(6)-Cl(1A)	3.019(2)	O(11)-Bi(5)-O(14)	93.58(19)
Si(1)–O(2)	1.621(6)	O(11)–Bi(5)–Cl(2)	88.86(15)
Si(1)-O(1)	1.626(6)	O(11)–Bi(5)–Cl(1)	174.24(15)
Si(1)–O(3)	1.636(6)	O(6)-Bi(5)-O(14)	90.46(19)
Si(3)–O(6)	1.621(5)	O(12)-Bi(6)-O(9)	87.5(2)
Si(3)–O(5)	1.633(5)	O(12)-Bi(6)-O(14)	90.71(19)
Si(3)–O(4)	1.651(5)	O(12)–Bi(6)–O(16)	75.4(2)
Si(5)–O(9)	1.613(5)	O(12)–Bi(6)–Cl(2)	86.35(14)
Si(5)–O(8)	1.621(5)	O(12)–Bi(6)–Cl(1A)	165.58(14)
Si(5)–O(7)	1.653(6)	O(14)–Bi(6)–Cl(1A)	76.60(12)
Si(7)–O(11)	1.620(5)	Cl(2)-Bi(6)-Cl(1A)	83.95(6)
Si(7)–O(12)	1.632(6)	Bi(1)–O(13)–Bi(2)	113.3(2)
Si(7)–O(10)	1.663(5)	Bi(1)-O(13)-Bi(3)	114.3(2)
		Bi(2)–O(13)–Bi(3)	114.0(2)
		Bi(5)-O(14)-Bi(4)	119.0(2)
		Bi(5)–O(14)–Bi(6)	116.1(2)
		Bi(4)-O(14)-Bi(6)	120.1(2)



Fig. 2. ORTEP diagram of cores of the two independent molecules of **2** with 50% probability. Most of the substituents on silicon atoms are omitted for the sake of clarity.

Me₃*Si*N unit ($\delta = 6.4$, 5.5, 2.5 ppm), whereas the rest are assigned for the O₃*Si*N part ($\delta = -72.2, -79.1, -83$ ppm), indicating that in each Bi₆Cl₂O₁₄Si₄ unit out of four, two silanetriol molecules are present in the same electronic environ-

ment. In compounds **2** and **3**, the ²⁹Si NMR chemical shifts for the O_3SiN silicon centers are shifted upfield compared to the values observed in the parent silanetriol (-67.3 ppm) [20]. The solid state structure of **3** has been



Fig. 3. ORTEP diagram of core 3 with 50% probability. Most of the substituents on silicon and bismuth atoms are omitted for the sake of clarity.

unambiguously established by single-crystal X-ray diffraction study (Table 1).

2.4. Structural description of 3

The pale yellow crystals of **3** were obtained from a hexane/THF mixture at room temperature over a period of two weeks. The ORTEP diagram of **3** is depicted in Fig. 3. Compound **3** crystallizes in the monoclinic space group $P2_1/n$ along with half of the molecule and one molecule of THF in the asymmetric unit. Selected bond distances and angles obtained for this compound are listed in Table 2. The molecular structure of **3** consists of a centrosymmetric Bi₁₂Cl₄O₂₈Si₈ core. The core structure of **3** contains two Bi₆Cl₂O₁₄Si₄ units that are fused together to generate a Bi₄Cl₂O₄Si₂ [Bi(6)–Cl(1A)–Bi(A5)–O(11A)– Si(7A)–O(12A)–Bi(6A)–Cl(1)–Bi(5)–O(11)–Si(7)–O(12)] 12membered ring (Fig. 2).

Each of these $Bi_6Cl_2O_{14}Si_4$ units is made up of four-(two Bi_2O_2 and one Bi_2ClO), six- (seven Bi_2O_3Si , one Bi_2ClO_2Si , one Bi_2ClO_2Si and one Bi_3O_3) and eight-membered rings (three $Bi_2O_4Si_2$, one Bi_3O_4Si , and one Bi₃ClO₃Si). The μ_3 -bridging oxygens O(13) and O(14) have markedly pyramidal and distorted trigonal planar geometries, which can be indicated by the sum of the Bi-O-Bi angles centered around O(13) ($\sum 342^\circ$) and O(14) $(\sum 355^\circ)$, respectively. Interestingly, these μ_3 -bridging oxygens lead to the formation of four- (two Bi2O2[Bi(2)-O(13)-Bi(1)-O(7); Bi(2)-O(13)-Bi(3)-O(10)] around O(13)and one Bi_2ClO [Bi(6)–O(14)–Bi(5)–Cl(2)]), six- (one Bi₂O₃Si [Si(5)-O(8)-Bi(4)-O(14)-Bi(6)-O(9)]around O(14), which are fused together to form another $Bi_{3}O_{3}[Bi(2)-O(7)-Bi(1)-O(13)-Bi(3)-O(10)])$ and eightmembered rings (Bi₃ClO₃Si [Bi(6)–O(9)–Si(5)–O(8)–Bi(4)– O(14)-Bi(5)-Cl(2)]). As shown in Fig. 3, the coordination geometry at Bi(1), and Bi(3) may be described as a distorted square pyramid with two silicon bonded μ_3 -bridging oxygen atoms, one μ_3 -bridging oxygen atom, one coordinated oxygen atom of a THF molecule, and a silicon bonded μ -bridging oxygen. The O–Bi–O angles around Bi(1) and Bi(3) are in the range of $67.7(2)-159.9(2)^{\circ}$ and $67.2(2)-165.3(2)^{\circ}$, respectively, which deviate slightly from the ideal value of 90°, indicating astereochemically active lone pair.

The coordination environment of Bi(2) is composed of three silicon bonded oxygen atoms, and one μ_3 -bridging oxygen, however the environment around Bi(4) consists of two silicon bonded oxygens, one μ_3 -bridging oxygen, and one coordinated oxygen atom of a THF molecule. Both Bi(2) and Bi(4) are in a distorted tetrahedral geometry. The O-Bi-O angles around Bi(2) and Bi(4) fall in the range of 68.1(2) to 140.6(2) and 73.5(2) to 158.4(2) which are strongly deviate from the ideal tetrahedral values (109.5°). The Bi(5) adopts a distorted trigonal bipyramidal geometry with one silicon bonded oxygen, one μ_3 -bridging oxygen, and one chloride at the equatorial sites and one silicon bonded oxygen and one chlorine at the apical sites, with an angle of $174.2(2)^{\circ}$. The rest of the angles at Bi(5) are in the range of $(77.8(1) \text{ to } 166.95(14)^\circ)$. The coordination environment around Bi(6) is made up of two silicon bonded oxygens, one μ_3 -bridging oxygen, one coordinated oxygen of a THF molecule, and two chloride in a distorted octahedral geometry. The O-Bi-Cl axis is quasi-linear (165.6(1)°) and the corresponding angles centered around Bi(6) are in the range from 75.4(2) to 163.2(2)°. The O-Si-O angles are within the range of $105.0(3)-113.3(2)^{\circ}$ for [O(6)-Si(3)-O(4) and O(11)-Si(7)-O(12) av. 108.5°], indicating the nearly ideal tetrahedral geometry for the silicon atoms.

The Bi-O bond distances in compound 3 vary in the range of 2.067(6) - 2.893(7) Å [Bi(2)-O(2) and Bi(1)-O(2L)], with an average value of 2.291(7) Å. The bond lengths involving the μ_3 oxygen centers are at the longer end of the range (2.139(5)-2.512(6) Å) for [Bi(1)-O(13) and Bi(3)-O(10) with an average value of 2.277(6) Å. and those to the μ oxygen centers are the shortest 2.067(6)-2.144(5) Å [Bi(2)-O(2) and Bi(6)-O(9) av. 2.10(6) Å]. The average Bi-O bond length in the framework is 2.189(6) Å which is remarkably shorter than the exocyclic Bi-O bond distances of 2.765(7) Å. The Si-O and Bi-Cl bond distances fall in the range of 1.613(5)-1.663(5) Å [Si(5)–O(9) and Si(7)–O(10)] (av. 1.632(6) Å) and 2.851(2)-3.019(2) Å [Bi(5)–Cl(2) and Bi(6)–Cl(1A) av. 2.93(2) Å] (sum of the atomic radii for Bi–Cl 2.87 Å) [24], respectively. Compared with Bi(OSiPh₃)₃(THF)₃, which shows a Bi-O bond distance of av. 2.495 Å, the average Bi–O distance in 3 is shorter by 0.204 Å. These Bi–O bond distances can be compared to those reported Bi-O bond distances {(av. 2.165 Å) for $[(tBuPO_3H)_{10}(tBuPO_3H)_2]$ $Bi_{14}O_{10} \cdot 3C_6H_6 \cdot 4H_2O$ [13b], {(av. 2.348 Å) for $Bi_8(\mu_4 - \mu_5)$ $O_{2}(\mu_{3}-O_{2}(\mu-OR) (R=OC_{6}F_{5})]$ [13c] and {(av. 2.346 Å) for $[Bi_{22}O_{26}(OSiMe_2tBu)_{14}]$ [13d,13e].

3. Conclusion

In summary, the single-crystal X-ray structure analysis of the first cubic polyhedral antimony(III) containing siloxane **2** is reported. Compound **3** represents an extremely soluble new bismuth(III) cluster containing chloride and siloxane ligands. In both of these compounds, antimony and bismuth atoms are in the formal oxidation state of +III with the M/Si ratio of 4:4 and 12:8, respectively.

4. Experimental

4.1. General procedure

All experimental manipulations were carried out under a dry nitrogen atmosphere, rigorously excluding air and moisture. The samples for spectral measurements were prepared in a drybox. Solvents were purified according to conventional procedures and were freshly distilled prior to use. Silanetriol [20], Sb(NMe₂)₃ [21], and Bi(NMe₂)₃ [22] were prepared according to the published procedures. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie, der Universität Göttingen. NMR spectra were recorded on Bruker Advance 500 MHz spectrometer. Chemical shifts are reported in ppm with reference to TMS (¹H and ²⁹Si). IR spectra were obtained on a Bio-Rad FTS-7 spectrometer as nujol mulls. Mass spectra were recorded on a Finnigan MAT system 8230 and a Varian MAT CH5 mass spectrometer by EI-MS methods. Melting points were measured on a HWS-SG 3000 apparatus and are uncorrected.

4.2. Synthesis and characterization of compound 2

To a stirred suspension of silanetriol (1.4 g, 4.28 mmol) in hexane (25 mL) and THF (1 mL), liquid $Sb(NMe_2)_3$ (1.09 g, 4.28 mmol) was added slowly at room temperature to produce a homogeneous solution. During the course of the reaction, evolution of dimethylamine was observed. The resulting clear solution was stirred for another 24 h at room temperature and then heated to reflux for 1 h. The reaction mixture was allowed to cool to room temperature and upon partial removal of the solvent in vacuo a slight turbid solution was obtained, which disappeared after gentle warming. The resulting solution was allowed to crystallize at room temperature to obtain colorless crystals of 2 after 4 days, yield 1.59 g, 83%. M.p. 386-388 °C (decomp); ¹H NMR (500 MHz, C₆D₆, TMS): $\delta = 0.25$ (s, 36H, Si(C H_3)₃), 1.23, 1.26 (d, J = 6.9 Hz, 48H, CH(C H_3)₂), 3.75 (sept, J = 6.9 Hz, 8H, CH(CH₃)₂), 6.99 (m, 12H, aromatic); ²⁹Si NMR (99 MHz, C₆D₆, TMS): $\delta = 4.4$ (*Si*Me₃), and -91 (SiO₃); IR (Nujol, KBr): $\tilde{v} = 1364$ (m), 1341 (w), 1318 (m), 1259 (m), 1249 (s), 1182 (s), 1106 (m), 1060 (s), 1043 (s), 996 (m), 959 (s), 944 (s), 906 (s), 892 (s), 838 (s), 801 (s), 754 (m), 722 (m), 682 (w), 643 (w), 595 (w), 583 (m), 546 (m), 484 (m), 445 (w), 401 (m) cm⁻¹; EIMS (70 eV): m/z (%): 1784 (100) $[M^+]$; Elemental analysis (%) calc. for C₆₀H₁₀₄N₄O₁₂Sb₄Si₈(1785.19): C, 40.37; H, 5.87; N, 3.14. Found: C, 39.56; H, 6.26; N, 2.64%.

4.3. Synthesis and characterization of compound 3

 $Bi(NMe_2)_3$ (1.46 g, 4.28 mmol) in hexane (10 mL) was slowly added to a stirred suspension of the silanetriol (1.4 g, 4.28 mmol) in hexane (10 mL) and THF (3 mL) at room temperature. During the course of the reaction, evolution of dimethylamine was observed. The resulting clear solution was stirred for another 24 h at r.t. and then heated to reflux for 1 h. The reaction mixture was allowed to cool to r.t. and upon partial removal of the solvent in vacuo a slight turbid solution was obtained, which disappeared after gentle warming. The resulting solution was allowed to crystallize at r.t. to obtain pale yellow crystals of **3** after two weeks, yield 0.71 g, 23%. M.p. >398 °C (decomp); ²⁹Si NMR (99 MHz, C₆D₆, TMS): $\delta = 6.4$, 5.5, 2.5 (*Si*Me₃), and -72.2, -79.1, -83 (*Si*O₃); IR (Nujol): $\tilde{\nu} = 1320$ (w), 1258 (s), 1245 (s), 1184 (m), 1105 (m), 1075 (w), 1044 (s), 956 (s), 917 (s), 887 (s), 835 (s), 801 (s), 751 (w), 722 (w), 684 (w), 641 (w), 599 (w), 544 (m), 501.41 (w), 484 (m), 419 (m) cm⁻¹; Elemental analysis (%) calc. for C₁₅₂H₂₇₂Bi₁₂Cl₄N₈O₃₆Si₁₆(5886.76): C, 31.01; H, 4.66; N, 1.90. Found: C, 30.78; H, 4.76; N, 2.00%.

4.4. Single-crystal X-ray structure determination of 2 and 3

Data for the compound 2 were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector and for the compound 3 were measured on a STOE-IPDS II diffractometer. Intensity measurements were performed on a rapidly cooled crystal. The structures were solved by direct methods (SHELXS-97) [25] and refined with all data by full-matrix least-squares on F^2 [26]. The hydrogen atoms of C-H bonds were placed in idealized positions and refined isotropically with a riding model, whereas the non-hydrogen atoms were refined anisotropically. In compound 2, the disordered isopropyl groups and the free THF solvent molecules were refined with distance and ADP restraints. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre: CCDC 281723 for 2 and CCDC 281724 for 3. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336 033; e-mail: deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005. 12.005.

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