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Hexa- and Trinuclear Organoantimony Oxo Clusters Stabilized by Organosilanols

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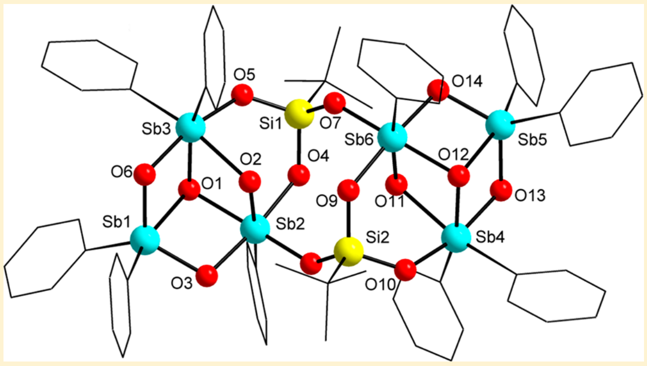
S *Supporting Information*

ABSTRACT: Reactions of Ph_2SbCl_3 with $RSi(OH)_3$ [where R = *tert*-Bu, *cyclo*-C_6H_{11}] and $Ph_2Si(OH)_2$ in toluene in the presence of triethylamine as a base were performed. Single-crystal X-ray structural elucidation of the products revealed the formation of hexanuclear antimony(V) and mixed-valent antimony (III/V) oxo-hydroxo clusters built up of an incomplete cubane subunit. Interestingly, in all the reactions, at least one Sb−C bond cleavage has been observed, leading to the formation of novel cluster assemblies $[(Ph_2Sb)_4(PhSb)_2(C_4H_9SiO_3)_2(O)_6(OH)_2]$ (**1**), $[(Ph_2Sb)_4(PhSb)_2(C_6H_{11}SiO_3)_2(O)_6(OH)_2]$ (**2**), $[(Ph_2Sb)(PhSb)_2(Ph_2SiO_2)_2(O)_3(OH)_2]^-Et_3NH^+$ (**3**), and $[(Ph_2Sb)_4(Sb)_2(Ph_2SiO_2)_2(O)_6(OH)_2]$ (**4**), respectively.



■ INTRODUCTION

Molecular clusters constructed from organoantimonates[1−5]/organosilanols containing motifs are a rarity despite potential applications of these compounds in biology, catalysis,[6,7] and in synthesizing model compounds for zeolites.[8] Recently, assemblies of a distorted Sb_4O_4 cubane cluster have been reported, obtained by reacting organostibonic acid with diorganosilanediol in 1:1 stoichiometry.[9] Further synthesis and self-assembly of a novel nonanuclear antimony phosphinate cluster involving Sb−C bond cleavage has also been reported.[10] It has to be mentioned here that reactions of diorgano/triorganoantimony halides with silver salts of acids have been carried out, leading to the isolation of diorganoantimony-based molecular clusters.[11] Considering the facile cleavage of Sb−C bonds[12,10] and the rarity of molecular clusters containing an Sb−O−Si framework, the reactions of diphenylantimony(V) trichlorides with organo silanetriols and diols were investigated. Recently, Beckmann et al. reported the synthesis and structural characterization of the first Sb(V)/Sb(III) mixed-valent cluster starting from an Sb(III) precursor.[13] A recent report on the promotion of phosphaalkyne cyclooligomerization by an Sb(V) to Sb(III) redox system[14] and the Beckmann's report on the isolation and structural characterization of a mixed-valent system motivated us to continue our work in synthesizing molecular architectures consisting of organoantimonates/organosilanols motifs. Hence, investigations on reactions of diorganoantimony trihalides with organo silanetriols {where R = *tert*-Bu (1) and *cyclo*-C_6H_{11} (2)} and diphenylsilanediol were carried out. Herein, the synthesis and structural characterization of hexa- and trinuclear organoantimony oxo clusters including a mixed-valent cluster is reported.

■ RESULTS AND DISCUSSION

Syntheses of **1**−**4** were carried out in toluene by reaction of Ph_2SbCl_3 with $RSi(OH)_3$ (R = *tert*-Bu/*cyclo*-hexyl) or with $Ph_2Si(OH)_2$ in the presence of triethylamine at room temperatures (Scheme 1). The compounds were analyzed using standard spectroscopic and analytical methods. IR spectra of **1**−**4** showed broad bands at 3300−3430 cm^{-1} indicating the presence of hydroxyl groups in the compounds. Isolated crystals of **1**−**4** showed poor solubility in common organic solvents, and hence, solution NMR studies could not be performed on crystalline samples. The crude products isolated were used for measuring ^{29}Si NMR (solution), which showed a single resonance signal (−21.19 and −22.07 ppm, respectively) for the products **1** and **2**, which corresponds to the presence of a silicon atom in a unique structural environment. The ^{29}Si NMR of the crude product in the reaction between diphenylantimony trichloride and diphenylsilanediol showed two signals that could correspond to the presence of a silicon atom in two different sets of environment. However, single-crystal X-ray characterization actually revealed the formation of two structurally different products **3** and **4**. The reaction mixture from which **3** and **4** were structurally characterized gave ^{29}Si solution NMR signals at −32.22 and −21.86 ppm. For the assignment of ^{29}Si NMR signals for **3** and **4**, our earlier published work[9] on the isolation of a cubane cluster stabilized by $Ph_2SiO_2^{2-}$ ligands was kept as a reference point wherein the chelating $Ph_2SiO_2^{2-}$ ligands showed a single resonance at $\delta = -29.5$ ppm. Hence, the signal at −32.22 ppm in this case was considered for the $Ph_2SiO_2^{2-}$ ligands present in the trinuclear

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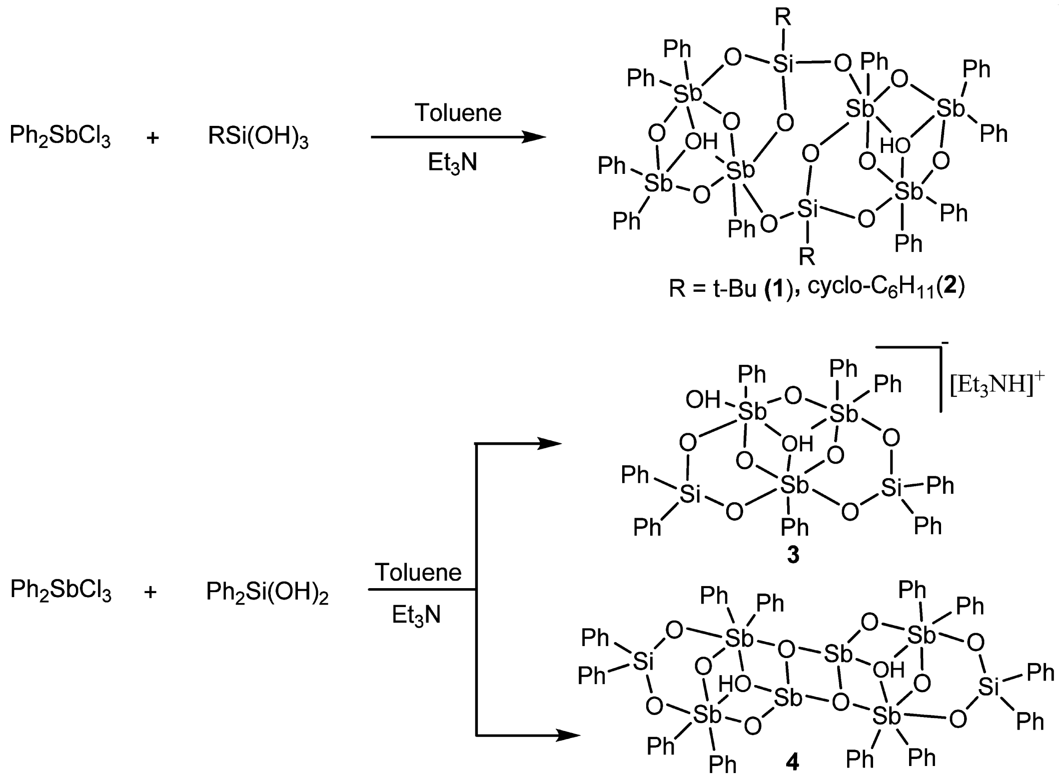
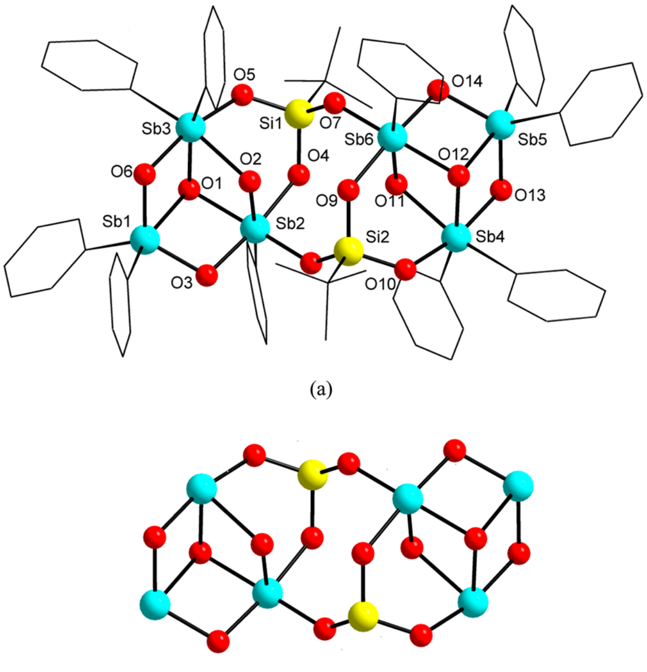
Scheme 1



cluster (**3**), while the other signal at −21.86 ppm, which is more upfield shifted, is assigned for $Ph_2SiO_2^{2-}$ ligands of the mixed-valent hexanuclear cluster (**4**).

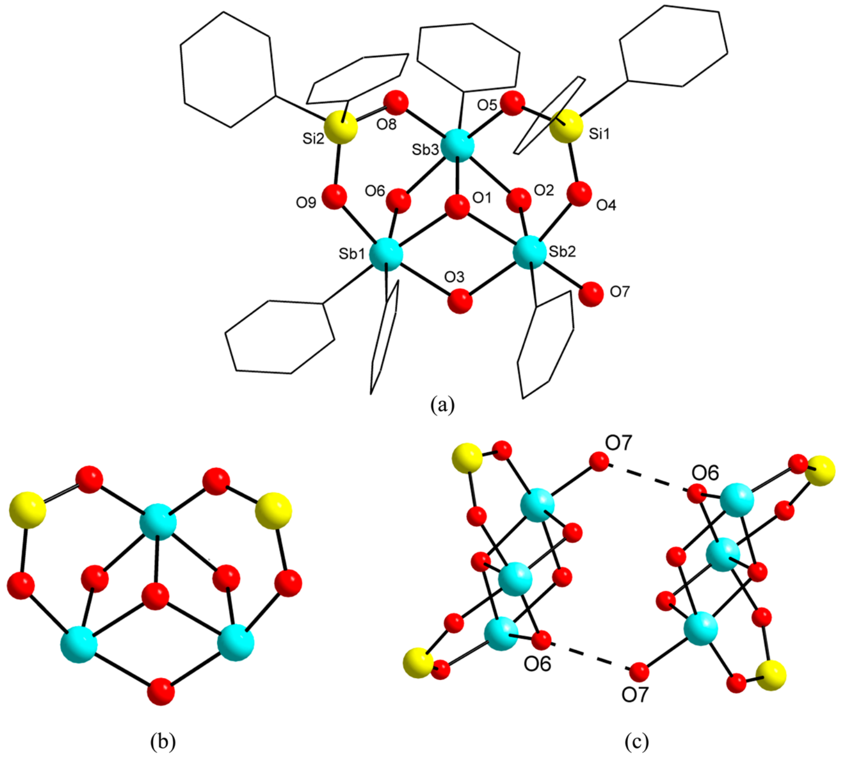
Single-crystal X-ray diffraction studies revealed that **1** and **2** are structurally similar. The molecular structure of **1** (Figure 1) is considered for discussion. **1** crystallizes in triclinic space group $P\bar{1}$. The structure of **1** can be described as follows: Two Sb_3O_4 units linked together by an organosilanol, binding in [3.111] mode. Each Sb_3O_4 unit can be described as a cube with a vertex missing. The three metal atoms are connected to each other by a μ_2-O group, and further, a μ_3-O bridges all the three metal atoms, hence making up the Sb_3O_4 unit. Within each Sb_3O_4 unit, two Sb atoms are present in diorgano forms, whereas the third metal atom is present as a monoorgano unit, which is obtained due to cleavage of an Sb−C bond from the diorganoantimony-based starting material. Such cleavage and formation of an in situ generated $R\text{-}SbO_3^{2-}$ unit have been reported recently in a phosphinate-based nonanuclear organoantimony oxo cluster.[10] The two silanols present bind the two trimers in a [3.111] mode, leading to the formation of a hexanuclear cluster in the solid state. For charge balance considerations, the μ_2-O is considered as oxo and the μ_3-O as hydroxyl groups. The effect of changing the R group on the silanol from *tert*-butyl to *cyclo*-hexyl did not have any effect on the structure of the end product obtained. Structural elucidation reveals the formation of a hexanuclear organoantimony silanolate in the case of **2** that is structurally similar to **1**. The Sb−O bond distances and Sb−O−Sb bond angles of the core are in the ranges of 1.91(18)−2.31(18) Å and 93.77(7)−109.90(8)°, respectively. Similarly, the Si−O and the silicon-bound O···Sb distances fall in the ranges of 1.62(19)−1.65(18) and 1.93(18)−1.97(18) Å, which are in close agreement with the literature values. Compounds containing Sb−O−Si motifs are a rarity in the literature. The structural characterizations of an antimony(III) bicyclic siloxane and a cubic Sb(III) compound containing Sb^{III}−O−Si^{IV} are some of the examples containing Sb−O−Si motifs that are known in the literature.[15,16] Recently, we reported the isolation of a cubane Sb_4O_4 cluster stabilized by diphenylsilanediol.[9] Molecular



(a)

(b)

Figure 1. (a) Molecular structure of **1**. (b) Core of **1**.



(a)

(b)

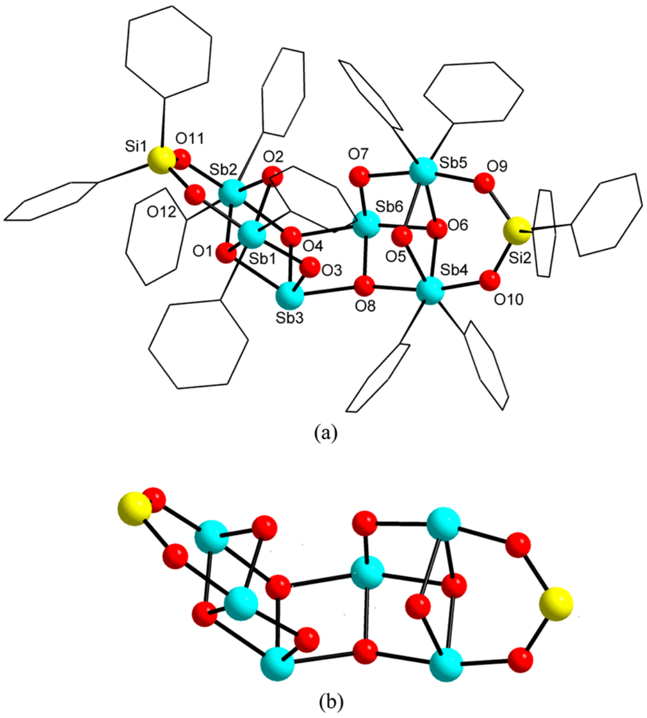
(c)

Figure 2. (a) Molecular structure of **3**. (b) Core of **3**. (c) Intermolecular O−H···O interaction.

clusters **1** and **2** reported herein are rare examples of compounds possessing Sb(V)−O−Si(IV) motifs.

3 crystallizes in monoclinic space group *P*2(1)/*n*. Structural elucidation reveals the formation of a trinuclear anionic cluster $[(Ph_2Sb)(PhSb)_2(Ph_2SiO_2)_2(O)_3(OH)_2]^-$ whose charge is balanced by the presence of an $[Et_3NH]^+$ cation (Figure 2). Interestingly, there are literature reports of reactions of diorganosilanediols with main group metals like gallium and aluminum in the presence of Et_3N/pyridine that lead to isolation of two different products, one being an anionic siloxane and the other being a neutral cluster.[17] A similar observation has been seen in this reaction also, wherein an Sb(V) state cluster and a mixed-valent Sb(V)/Sb(III) cluster have been isolated and structurally characterized. The structural description of **3** is as follows: an Sb_3O_4 core stabilized by two diorganosilanediols binding in [2.11] mode. The Sb_3O_4 unit present in **3** is similar to the unit that is found in **1**, the formation of a broken cubane with a vertex missing. The Sb metal atoms are bridged by three μ_2-O and a μ_3-O keeping the Sb_3O_4 motif intact. The interesting aspect about the structure is the presence of two monoorganoantimony groups formed by dearylation and one Sb atom present in the diorgano form. In fact, this cluster represents a state wherein an in situ generated R-SbO_3^{2-} unit and $RSb(OH)O_2^-$ (which could be a forerunner to $RSbO_3^{2-}$) are present. The anionic trinuclear organoantimony cluster charge is balanced by the presence of a triethylammonium cation. Further analysis of the solid-state packing revealed the presence of strong O−H···O interactions with a 2.586 Å bond length ($O_6 \cdots O_7$) stabilizing the trinuclear cluster in to a hexanuclear assembly. The interactions involved are shown in Figure2c.

Along with **3**, a crystal of different morphology in very small amounts was observed repeatedly. Structural characterization revealed the formation of a mixed-valent hexanuclear organoantimony cluster (Figure 3). **4** crystallizes in monoclinic space group *P*2(1)/*c*. The structure of **4** can be described as follows. Again, the molecular cluster consists of two Sb_3O_4 units connected along an Sb−O edge. The Sb metal atoms that are connected are Sb(III) centers, and hence, two Sb(III) metal atoms are present in **4**. The Sb(III) centers are 4-coordinate. The two other Sb metals in each Sb_3O_4 unit are Sb(V) and are



(a)

(b)

Figure 3. (a) Molecular structure of **4**. (b) Core of **4**.

Table 1. X-ray Data Collection Parameters for 1−4

	1	2	3	4
formula	$C_{68}H_{68}O_{14}Sb_6Si_2$	$C_{72}H_{72}O_{14}Sb_6Si_2$	$C_{54}H_{55}O_9NSb_3Si_2$	$C_{79}H_{68}O_{12}Sb_6Si_2$
M	1895.90	1948.04	1283.45	1996.08
T (K)	298(2)	298(2)	298(2)	298(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
crystal system	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$	$P2(1)/c$
a (Å)	11.125 (8)	12.728(4)	18.9322(15)	11.375(10)
b (Å)	12.049 (9)	13.015(4)	28.524(2)	35.748(3)
c (Å)	26.136(2)	13.544(4)	24.7911(19)	19.229(14)
α (deg)	85.50(10)	108.884(4)	90°	90°
β (deg)	79.73(10)	116.854(4)	102.7550(10)	110.493(4)
γ (deg)	78.72(10)	95.664(4)	90°	90°
v (Å^3)	3377.1 (4)	1812.4(9)	13057.4(17)	7324.7(10)
z	2	1	8	4
D_{calcd} (g cm^{-3})	1.864	1.785	1.308	1.812
μ (mm^{-1})	2.465	2.299	1.317	2.276
F(000)	1844	950	5128	3896
θ range (deg)	1.59−26.05	1.73−24.98	1.10−25.09	1.14−28.28
index range	$-13 \le h \le 13$	$-15 \le h \le 15$	$-22 \le h \le 22$	$-15 \le h \le 14$
	$-14 \le k \le 14$	$-15 \le k \le 15$	$-33 \le k \le 33$	$-47 \le k \le 46$
	$-32 \le l \le 32$	$-16 \le l \le 16$	$-29 \le l \le 29$	$-25 \le l \le 24$
reflections collected	35 100	17 302	125 092	84 932
data/parameters	13 211/817	6338/424	23 117/1249	17 576/593
goodness-of-fit (GOF) on F^2	1.035	1.055	1.095	1.148
R_1 [$I > 2\sigma$]	0.0245	0.0624	0.0853	0.0353
wR_2	0.0636	0.1464	0.2597	0.0761

held together by diphenylsilanediol by a [2.11] mode of binding. Overall, the cluster has four μ_2-O and four μ_3-O making up the cluster core. Of the four μ_3-O, two μ_3-O connect the three metal atoms in an Sb_3O_4 unit while the other two μ_3-O are present in the edge that links the two Sb_3O_4 units. This isolation of a mixed-valent compound starting from an Sb(V) precursor is very interesting since no reducing agents were used in the reaction. Beckmann et al. recently reported the synthesis and structural characterization of the first mixed-valent Sb clusters by carrying out controlled hydrolytic cleavage of highly soluble and bulky 2,6-$Mes_2C_6H_3SbCl_2$ wherein Sb atoms are present in a +3 oxidation state.[13] Herein, we present for the first time the formation of a mixed-valent organoantimony cluster obtained by starting from antimony(V) starting material. Reduction, followed by cleavage and elimination of the two phenyl groups or vice versa, has resulted in this unique molecular cluster. Since the yield of the isolated cluster is poor, the corresponding oxidized products are difficult to envisage. The structural characterization of the product proves the formation of a mixed-valent cluster, so the reduction process as well the phenyl cleavage does happen, though in very small amounts. This kind of reduction, though, is unknown in organoantimony compounds, an example from a ruthenium complex wherein Ru(V)-to-Ru(III) reduction has been proposed by the triethylamine reagent used in the synthesis that would be the reductant undergoing oxidation to acetaldehyde and diethyl amine.[18] Since triethylamine is also used as a base during the synthesis of **3**, probably a slight excess of triethylamine present might have behaved as the reductant, though in very small amounts since **4** is isolated in really low yields repeatedly. Recently reduction of Sb(V) to Sb(III) has been shown to catalyze promotion of phosphaalkyne cycloligomerization.[14] The average Sb^V−O and Sb^{III}−O bond distances of **4** fall in the ranges of 1.955(2)−2.159(2) and 1.966 (2)−2.207(2) Å, respectively. These values are in good agreement with the bond lengths of the mixed-valent cluster reported recently by Beckmann et al.[13]

■ CONCLUSION

Novel hexa- and trinuclear organoantimony oxo-hydroxo clusters have been assembled by reaction of organoantimony halides with silanols. To the best of our knowledge, synthesis of a mixed-valent cluster through reduction of the Sb(V) starting material is reported herein for the first time in organoantimony literature.

■ EXPERIMENTAL SECTION

General Procedures. Ph_2SbCl_3, *tert*-butyl silanetriol, and *cyclo*-hexyl silanetriol were synthesized using literature procedures.[19] Solvents and other common reagents were purchased from commercial sources. Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. Elemental analysis was performed on a Flash EA series 1112 CHNS analyzer. The Si^{29} NMR spectra were recorded on a Bruker Ultrashield 400 MHz instrument.

General Synthetic Procedure. The stoichiometric amounts of Ph_2SbCl_3 and $RSi(OH)_3$ [R = *t*-Bu or *cyclo*-C_6H_{11}] or $Ph_2Si(OH)_2$ were dissolved in 50 mL of toluene in the course of 20 min. Triethylamine was added, and stirring was continued for another 6 h at room temperature. The resultant solution was filtered and evaporated under reduced pressure to yield a white powder. Block type crystals were formed from slow diffusion of hexane into toluene solution after several days. The crystals for the compounds **3** and **4** are obtained from the same reaction mixture. The stoichiometry and the amounts of the reagents used in each case are given below.

1: Ph_2SbCl_3 (0.42 g, 1.10 mmol), *tert*-$BuSi(OH)_3$ (0.15 g, 1.10 mmol), Et_3N (0.11 g, 3.30 mmol); yield 0.21 g (60.5%). m.p. > 300 °C. Elemental anal. calcd. for $C_{68}H_{68}O_{14}Sb_6Si_2$: C, 43.07; H, 3.61. Found: C, 43.16, H, 3.65. IR (cm^{-1}, KBr pellet): υ(cm^{-1}) 3419(b),

Table 2. Bond Length (Å) and Bond Angle (deg) Parameters for 1–4

1	2	3	4
Sb1–O6 = 1.9107 (18)	Sb1–O6 = 1.9000(6)	Sb1–O6 = 1.991(7)	Sb1–O1 = 2.124(2)
Sb3- O2 = 2.2185 (18)	Sb3–O2 = 2.205(5)	Sb3–O2 = 2.026(7)	Sb1–O12 = 1.955(2)
Sb2–O3 = 2.0043(17)	Sb2–O3 = 2.005(5)	Sb2–O3 = 2.129(7)	Sb1–O2 = 2.159(2)
Sb1–O1 = 2.3132(18)	Sb1–O1 = 2.293(6)	Sb1–O1 = 2.18(7)	Sb1–O3 = 2.010(2)
Sb2–O1 = 2.0447(18)	Sb2–O1 = 2.042(5)	Sb2–O1 = 2.099(7)	Sb3–O3 = 1.966(2)
Sb3–O1 = 2.0515(17)	Sb3–O1 = 2.031(6)	Sb3–O1 = 2.089(7)	Sb3–O8 = 2.153(2)
Sb2–O8 = 1.9374(18)	Sb2–O7* = 1.938(5)	Sb2–O7 = 1.949(7)	Sb3–O1 = 2.207(2)
Sb3–O5 = 1.9758(18)	Sb3–O5 = 1.959(5)	Sb3–O5 = 1.963(7)	Sb3–O4 = 2.027(2)
Sb2–O4 = 1.9890(17)	Sb2–O4 = 1.971(5)	Sb2–O4 = 1.967(7)	Sb2–O1 = 2.025(2)
Si1–O4 = 1.6527(18)	Si1–O4 = 1.646(6)	Si1–O4 = 1.627(7)	Sb2–O2 = 2.142(2
Si1–O5 = 1.6253(19)	Si1–O5 = 1.610(6)	Si1–O5 = 1.619(8)	Sb2–O4 = 2.116(2)
Si1–O7 = 1.6373(19)	Si1–O7 = 1.627(6)	Sb1–O6–Sb3 = 104.6(3)	Sb2–O11 = 1.958(2)
Sb1–O6–Sb3 = 109.90(8)	Sb1–O6–Sb3 = 109.8(3)	Sb2–O2–Sb3 = 103.1(3)	Sb1–O1–Sb2 = 107.16(10)
Sb2–O2–Sb3 = 101.97(7)	Sb2–O2–Sb3 = 101.8(2)	Sb1–O3–Sb2 = 102.9(3)	Sb1–O2–Sb2 = 101.87(9)
Sb1–O3–Sb2 = 108.51(8)	Sb1–O3–Sb2 = 109.6(2)	Sb1–O1–Sb2 = 106.0(3)	Sb1–O3–Sb3 = 107.45(11)
Sb1–O1–Sb2 = 93.77(7)	Sb1–O1–Sb2 = 94.9(2)	Sb1–O1–Sb3 = 97.5(3)	Sb2–O1–Sb3 = 102.93(10)
Sb1–O1–Sb3 = 95.08(7)	Sb1–O1–Sb3 = 96.0 (2)	Sb2–O1–Sb3 = 97.0(3)	Sb2–O4–Sb3 = 106.17(10)
Sb2–O1–Sb3 = 109.04(8)	Sb2–O1–Sb3 = 109.6(3)	Sb2–O2–Sb3 = 103.1(3)	Sb3–O8–Sb6 = 105.43(10)
Sb2–O2–Sb3 = 101.97(7)	Sb2–O2–Sb3 = 101.8(2)	O4–Si1–O5 = 112.2(4)	O8–Sb3–O4 = 74.58(9)
O4–Si1–O5 = 109.49(10)	O4–Si1–O5 = 111.2(3)		O4–Sb6–O8 = 74.83(9)

3051(w), 2925(m), 2848(s), 1577(m), 1473(s), 1435(m), 969(s), 936(s), 804(s), 733(m), 684(m). ^{29}Si NMR (in $CDCl_3$): δ −21.19 ppm

2: Ph_2SbCl_3 (0.23 g, 0.61 mmol), *cyclo*-$C_6H_{11}Si(OH)_3$ (0.10 g, 0.61 mmol), Et_3N (0.18 g, 1.84 mmol); yield 0.12 g (60.3%). m.p. > 300 °C. Elemental anal. calcd. for $C_{72}H_{72}O_{14}Sb_6Si_2$: C, 44.39; H, 3.72. Found: C, 44.21, H, 3.74. IR (cm^{-1}, KBr pellet): 3325(b), 3051(m) 2903(m), 2843(s), 1478(m), 1429(s), 1067(m), 996(s), 941(s), 881(s), 728(m), 689(m), 481(S). ^{29}Si NMR (in $CDCl_3$): δ −22.07 ppm.

3: Ph_2SbCl_3 (0.30 g, 0.78 mmol), $Ph_2Si(OH)_2$ (0.17 g, 0.78 mmol), Et_3N 0.238g (2.30 mmol); yield 0.21 g (63.6%). m.p. > 300 °C. Elemental anal. calcd. for $C_{54}H_{55}NSb_3O_9Si_2$: C, 50.53; H, 4.31; N, 1.089. Found: C, 50.38, H, 4.39; N, 1.13. IR (cm^{-1}, KBr pellet): 3430(b), 3046(w), 3002(m), 1478(s), 1429(m), 1111(s), 958(s), 903(s), 739(m), 700(m). ^{29}Si NMR (in $CDCl_3$): δ −32.22 ppm.

4: Yield 0.015 g (5.7%). m.p. > 300 °C. Elemental anal. calcd. for $C_{79}H_{68}O_{12}Sb_6Si_2$: C, 47.48; H, 3.53. Found: C, 47.38, H, 3.56. IR (cm^{-1}, KBr pellet): 3414(b), 3041(w), 2997(m), 1589(m) 1479(s), 1430(m), 1112(s), 1073(s), 953(s), 904(s), 728(m), 690(m). ^{29}Si NMR (in $CDCl_3$): δ −21.86 ppm.

X-ray Crystallography. Crystal data parameters are given in Table 1. Selected bond lengths and bond angles for **1–4** are given in Table 2. Single-crystal X-ray data collection were carried out at 298 K on a Bruker Smart Apex CCD area detector system (λ (Mo Kα) = 0.71073 Å) with a graphite monochromator. The data were reduced using SAINT PLUS, and the structures were solved using SHELXS-97[20] and refined with SHELXL-97.[21] The structures were solved by direct methods and refined by full-matrix least-squares cycles on F^2. All non-hydrogen atoms were refined anisotropically.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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