ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 1137–1143 1137
DOI: 10.1021/om900942q

Isolation of Tetranuclear Organoantimony Oxo Clusters and Hexa-decanuclear Polyoxostibonates

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Received October 27, 2009

Reaction of phenolic pyrazolyl ligands with arylstibonic acids afforded two novel tetranuclear clusters $[(p\text{-}X\text{-}C_6H_4Sb)_4(O)_5(OH)_2(HPhPzR^1)_4]$ (where X = Cl, R^1 = Ph (**1**); X = Br, R^1 = Ph (**2**); X = Br, R^1 = t-Bu (**3**)) and $[(p\text{-}Br\text{-}C_6H_4Sb)_4(PhPz)_4(O)_4]$ (**4**). Depending on the steric bulk of the group present on the pyrazole ring, either one (**1**−**3**) or two (**4**) of the ring nitrogens have been found to coordinate to the metal atoms. Remarkably, when 3,5-DMPz is reacted with arylstibonic acid, hexa-decanuclear polyoxostibonates $[(p\text{-}X\text{-}C_6H_4Sb)_{16}(O)_{28}(OH)_8](3,5\text{-}DMPz)_6$ (X = Cl (**5**), Br (**6**)) have been isolated.

Introduction

Synthesis, structure, and reactivity of organostibonic acids[1] are less studied compared to the analogous compounds of phosphorus[2] and arsenic[3] despite potential applications of organoantimony compounds in the field of catalysis[4] and biology.[5] As arylstibonic acids are poorly soluble in most of the common organic solvents, their structures in the solid state have been a matter of debate. Earlier reports by Schmidt, Doak, and Bowen using molecular weight measurements[1] and ^{121}Sb Mössbauer spectroscopy[6] suggested that arylstibonic acids exist with a high degree of association in the solid state and that the geometry around the Sb atom is trigonal bipyramidal. Recently Beckmann et al. reported the controlled hydrolysis of $2,6\text{-}Mes_2C_6H_3SbCl_4$ under basic conditions, leading to the isolation and structural characterization of the first molecular arylstibonic acid,[7] which crystallized as a dimer in the solid state with the geometry around the Sb atoms being trigonal bipyramidal, as predicted by earlier studies. The reactivity of organostibonic acid toward strong acids and bases has been investigated, unraveling the unusual reactivity of organostibonic acid compared to phosphorus and arsenic analogues.[8] Further, the ability of organostibonic acid to act as an inorganic cryptand incorporating transition metal and alkali metals in their cavities has also been reported recently.[9] The isolation of these reverse-keggin-type structures draws interesting parallels to well-established POM chemistry reported by Müller,[10] Pope,[11] and others.[12] Further reactions of organostibonic acids with phosphonic acid[13] and silanols[14] have been carried out, leading to the isolation of novel organoantimony oxo clusters. It is of interest to mention that an organoantimony phosphonate cluster has been shown to act as a proligand for synthesizing multinuclear cobalt clusters using solvothermal reaction conditions. Antimony oxo clusters have also been studied in the gas phase or condensed phase by mass spectrometry,[15] and it has been

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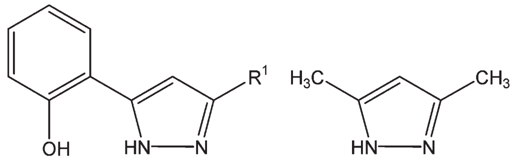
Chart 1



I

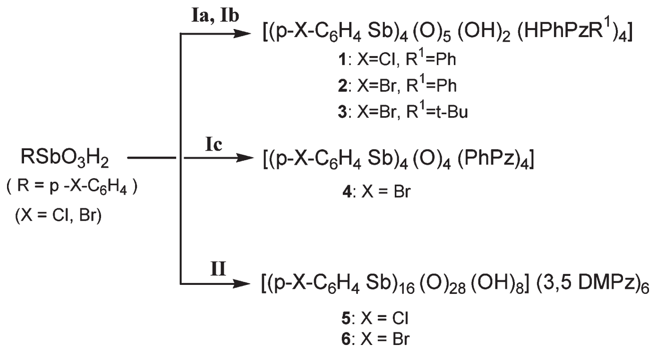
H_2PhPzR^1

II

3,5 DMPz

Ia: R^1 = Ph
Ib: R^1 = t-Bu
Ic: R^1 = H

Scheme 1



reported that at room temperature the stable solid phase of Sb_2O_3 is the cubic senarmontite, which contains a Sb_4O_6 molecule,[16] whereas the high-temperature orthorhombic phase valentinite has a polymeric sheet built up of eight-membered Sb_4O_4 rings.[17] Generally in these clusters antimony atoms are present in both the III and V state of oxidation, but at higher oxygen concentrations it has been shown that the formation of oxide clusters containing antimony atoms solely in the V state of oxidation is favored.[18] Synthesis and structural characterization of the first polyoxoantimonate $[Sb_8O_{12}(OH)_{20}]^{4-}$ devoid of any Sb−C bonds were reported by Yagasaki et al,[19] which was followed by the isolation of polyoxoantimonates built up from an Sb_4O_{16} core.[20] Despite the rich structural variations and utility of organoantimony oxo clusters, the reactions of arylstibonic acid with ligands containing mixed N,O-donor or N,N-donor atoms have not been investigated.

Herein, we report the synthesis and structure of the products (**1**−**6**) obtained on the reaction of organostibonic acid with pyrazolyl ligands having substitution at the 3,5-positions. The ligands chosen are depicted in Chart 1. These ligands have been utilized for synthesizing multinuclear transition metal clusters, some of which possess interesting magnetic properties.[21]

Results and Discussion

The general synthetic methodology adopted (Scheme 1) and the standard spectroscopic and analytical data for **1**−**6** are given in the Experimental Section. Crystals suitable for single-crystal X-ray diffraction for **1**−**6** were obtained either by slow evaporation of toluene or by a diffusion method using dichloromethane or chloroform/hexane. Crystals of **1** and **4** had poor solubility in common organic solvents, while **2**, **3**, **5**, and **6** were soluble in dichloromethane, chloroform, toluene, and xylene. ^1H NMR spectra (in $CDCl_3$ solution for **2**, **3**, **5**, and **6**) showed the appearance of multiplets from 6.7 to 7.8 ppm, corresponding to aromatic groups present. For compounds **5** and **6** signals at 1.3 ppm are assigned to pyrazole methyl groups. IR spectra of the compounds (except for **4**) exhibit broad peak around 3300−3400 cm^{-1}, indicating the presence of hydroxyl groups.

The crystal structure of **1** (X = Cl) and **2** (X = Br) revealed the formation of a tetranuclear organoantimony oxo cluster, $[(p\text{-}X\text{-}C_6H_4Sb)_4(O)_5(OH)_2(HPhPzR^1)_4]$. Clusters **1** and **2** crystallize in triclinic space group $P\bar{1}$ with varying solvent of crystallization, namely, toluene in **1** and chloroform in **2**. Since the cluster cores of **1** and **2** are identical, the structure of **1** is considered for discussion (Figure 1). It can be visualized as being build up of two Sb_3O_3 rings, which are nearly perpendicular to each other, sharing a Sb_2O unit. Four ligands were found coordinating to the metal atoms in a chelating mode of binding through the phenolic oxygen and the nitrogen of the pyrazole ring, while the other N atom is noncoordinating. All Sb atoms lie at the center of an octahedron with the CO_4N coordination mode. Two sets of Sb atoms are found in the cluster. The first set of Sb atoms, Sb1 and Sb4, are connected between themselves and to the two other Sb atoms by an oxo bridge; the fourth coordination is to the deprotonated oxygen of the phenolic group, with the fifth and the sixth coordination to the pyrazole nitrogen and the halophenyl carbon completing the primary coordination sphere. The other set of two Sb atoms are connected to the neighboring Sb atoms by oxo bridges, with coordination from the phenolic oxygen and the fourth and fifth coordinations from the nitrogen, the carbon of the pyrazole, and the halophenyl ring, respectively. The sixth coordination is to a terminal O atom, which on the basis of charge neutrality conditions is considered to be present as a terminal hydroxyl group. The Sb−O distances fall in the range 1.928(3) to 1.965(2) Å. The phenolic oxygen to Sb distance falls in the range 2.000(3) to 2.005(3) Å. The Sb−N distances fall in the range 2.170(3) to 2.187(3) Å. The Sb−O (hydroxyl) distances fall in the range 1.942(3) to 1.960(2) Å. Cluster **1** cocrystallizes with a molecule of the ligand and toluene in the crystal lattice. It should be mentioned here that the tetranuclear clusters (**1** and **2**) are similar to a recently reported triorganoantimony phosphinate cluster, $[(Ph_3Sb)_2(\mu\text{-}O)(cycPO_2)_2]$,[22] except that in the present case P atoms have been replaced by Sb atoms, leading to the formation of a tetranuclear cluster. The Sb−O distances in **1** are shorter than the phenolic oxygen to Sb distance, similar to the

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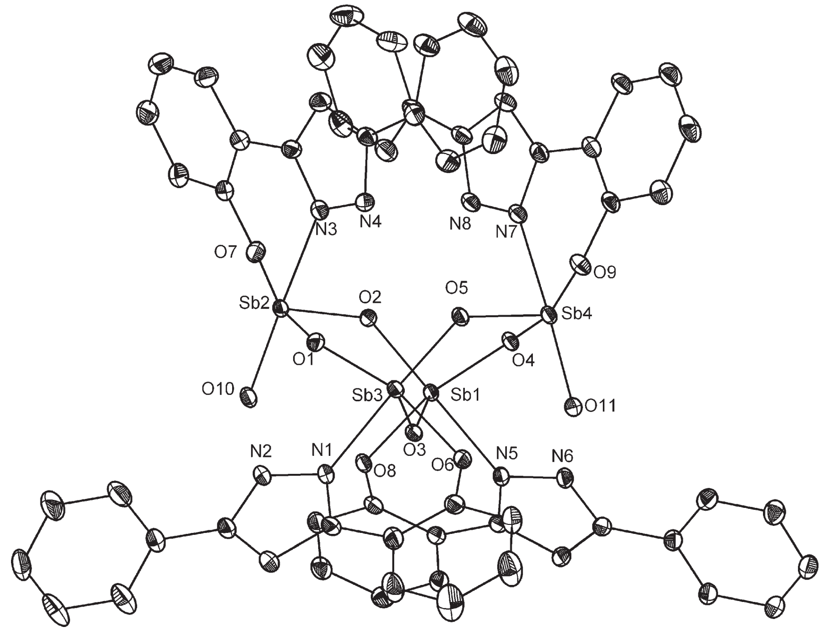

Figure 1. Molecular structure of **1** with thermal ellipsoids shown at 30% probability. The p-Cl-phenyl group on the Sb atoms and a molecule of free ligand that cocrystallized with **1** have been removed for clarity. Selected bond lengths (in Å) and bond angles (in deg): Sb1−O1 = 1.928(2), Sb1−O3 = 1.965(2), Sb1−O5 = 1.953(2), Sb1−O6 = 2.022(2), Sb2−O1 = 1.948(2), Sb2−O2 = 1.949(2), Sb2−O7 = 2.005(2), Sb2−O10 =1.962(2), Sb3−O2 = 1.947(2), Sb3−O3 = 1.958(2), Sb3−O4 = 1.938(2), Sb3−O8 = 2.025(2), Sb4−O4 = 1.942(2), Sb4−O5 = 1.961(2), Sb4−O11 = 1.960(2), Sb4−O9 = 2.000(2), Sb1−N1 = 2.187(3), Sb2−N3 = 2.186(3), Sb3−N5 = 2.170(3), Sb4−N7 = 2.173(3), O1−Sb1−O5 = 97.30(9), O1−Sb1−O3 = 94.60(9), O5−Sb1−O3 = 92.33(9), O1−Sb2−O2 = 92.71(9), O2−Sb3−O3 = 93.43(9), O4−Sb4−O5 = 92.66(9), O1−Sb1−N1 = 84.40(10), O4−Sb3−N5 = 85.13(9), Sb1−O1−Sb2 = 137.01(12), Sb1−O5−Sb4 = 132.71(12), Sb3−O3−Sb1 = 130.26(11), Sb3−O4−Sb4 = 134.47(12), Sb3−O2−Sb2 = 134.85(12).

triorganoantimony phosphinate cluster, where the μ-O to Sb distances have been reported to be shorter than the Sb−O distances from the phosphinate ligands. The Sb−O (hydroxyl) distances in **1** also fall in the range previously reported in the literature.[22]

Single-crystal X-ray elucidation studies for **3** revealed the formation of a tetranuclear organoantimony oxo cluster, isostructural to **1** and **2**. Hence the change in the group present at the 5-position of the pyrazolyl ligand from a phenyl to a *tert*-butyl had no effect on the structure of the product on reaction with arylstibonic acids. In further efforts to understand the steric effects on the reaction products, we carried out the reaction of p-Br-phenylstibonic acid with 3-(2-hydroxyphenyl)pyrazole. X-ray studies of the resulting product revealed the formation of a neutral tetranuclear organoantimony oxido cluster, [(p-Br-$C_6H_4Sb)_4(PhPz)_4(O)_4$] (**4**), which crystallizes in monoclinic space group *P*2(1)/*n* (Figure 2). Coordination geometry around each Sb atom is octahedral. All four Sb atoms lie in almost the same plane bridged through oxo groups, leading to the formation of an eight-membered Sb_4O_4 ring. The structure of **4** can be visualized as being built from two Sb_2O units held together by two oxo bridges. Each Sb_2O unit is a part of two Sb_2ON_2-containing five-membered rings, which are nearly perpendicular to each other. Each Sb_2O unit consists of two dianionic ligands with each ligand exhibiting both chelating (O,N-donors) and bridging modes of binding (N,N-coordination mode). The Sb−O distances fall in the range from 1.936(3) to 1.955(3) Å. The phenolic oxygen to Sb distance falls in the range 1.981(3) to 2.006(3) Å. The Sb−N distances fall in the range 2.111(3) to 2.216(4) Å.

Arylstibonic acid when reacted with a phenolic pyrazolyl ligand leads to the formation of a novel organoantimony oxo cluster. In the case of **1**−**3** only one N atom of the pyrazole ring participates in binding to the Sb atom, while the other N is noncoordinating. When a sterically less demanding group is present on the 5-position of the pyrazole ring, it acts as a bridging ligand, coordinating through both ring nitrogens, leading to the formation of a tetranuclear cluster (**4**) structurally different from **1**−**3**. This observation prompted us to investigate the reaction of arylstibonic acids with pyrazole devoid of any oxo donor substitution on the 3- and 5-positions. Hence the reaction of arylstibonic acid with 3,5-dimethylpyrazole (3,5-DMPz) was carried out following similar procedures to that of **1**−**4**. Single-crystal X-ray studies for **5** and **6** revealed the formation of hexa-decanuclear organoantimony oxo clusters [(p-X-$C_6H_4Sb)_{16}(O)_{28}(OH)_8$](3,5-DMPz)$_6$ (X = Cl (**5**), Br (**6**)), which crystallize in monoclinic space group *P*2(1)/*n*. Since **5** and **6** are isostructural, the structure of **5** is considered for discussion (Figure 3). The geometry around each antimony is octahedral, with a O_5C coordination mode. Four Sb_3O_3 and two Sb_2O_2 rings are found in **5**, which are held together by oxo bridges. Each Sb_3O_3 ring is capped by a μ_3-oxygen, reminiscent of O-capped clusters previously reported for similar organotin compounds.[23] The Sb_3O_3 units along with the capping μ_3-oxygen atom present in **5** can also be visualized as a cube with a vertex missing. Of the 36 oxo groups present in **5**, 28 are μ_2-bridging, while the other eight oxygen atoms are μ_3-bridging to the metal centers. These eight μ_3-bridging oxygen atoms are considered to be part of hydroxyls for charge neutrality considerations. The polyoxostibonate core is encapsulated

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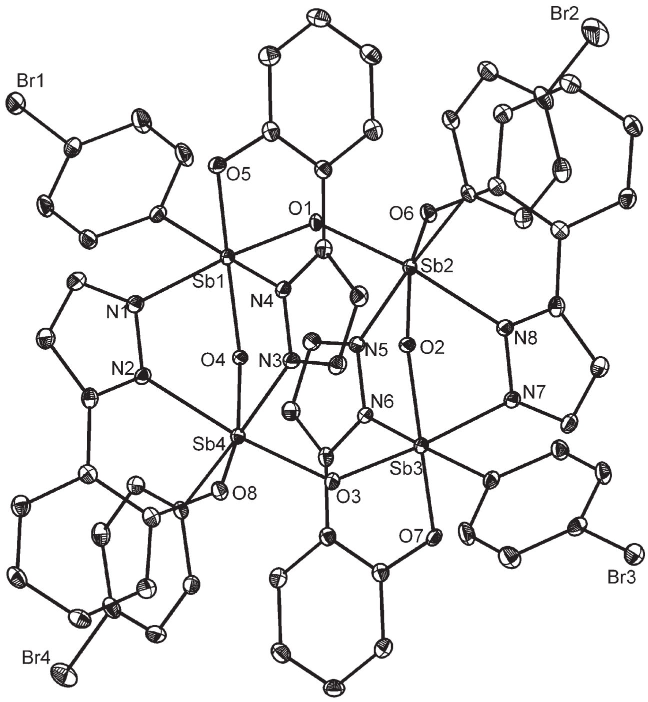

Figure 2. Molecular structure of **4** with thermal ellipsoids shown at 30% probability. Selected bond lengths (in Å) and bond angles (in deg): Sb1−O1 = 1.948(19), Sb1−O4 = 1.945(19), Sb1−N1 = 2.216(2), Sb1−N4 = 2.113(2), Sb2−O1 = 1.934(19), Sb2−O2 = 1.947(19), Sb2−N5 = 2.150(2), Sb2−N8 =2.166(2) Sb3−O2 = 1.942(19), Sb3−O3 = 1.948(19), Sb3−N6 = 2.110(2), Sb3−O7 = 1.985(2), Sb4−O3 = 1.940(19), Sb4−O4 = 1.953(19), Sb4−N2 = 2.163(2), Sb4−N3 = 2.146(2), O4−Sb1−O1 = 94.82(8), O1−Sb2−O2 = 100.86(8), O2−Sb3−O3 = 95.53(8), O3−Sb4−O4 = 101.88(8), Sb2−O1−Sb1 = 132.21(10), Sb3−O2−Sb2 = 120.91(10), Sb1−O4−Sb4 = 120.63(10), Sb4−O3−Sb3 = 131.58(10).

by 16 p-Cl-phenyl groups. A further three molecules of 3,5-DMPz crystallize in the asymmetric unit; hence six molecules of 3,5-DMPz crystallize along with the neutral hexa-decanuclear polyoxostibonate. The Sb−O distances in **5** fall in the range from 1.931(5) to 2.149(5) Å. The Sb−C distances fall in the range 2.107(8) to 2.129(10) Å.

The structure of **5** can also be visualized in polyhedral arrangements. Each Sb lies at the center of the polyhedron; three such polyhedra share two of its edges with the neighboring polyhedron, forming a triad. Each triad shares two edges with its neighboring triad on both sides, forming a cyclic framework built up of four triads. Further, two polyhedra share an edge and form dimers. Two such dimers are present in **5**; one above and the other below the central polyhedral arrangement formed by the four triads, leading to the formation of a closed-cage-like framework. The dimers are connected to the triads by three corner- and one edge-sharing polyhedra, resulting in the formation of eight triangular and four pentagonal faces in the cluster. It is well known that polymeric arylstibonic acids are insoluble white powders, and hence structural information is limited. Structures **5** and **6** can be considered as partially anhydrous forms of arylstibonic acid. Although an earlier literature report based on Mössbauer spectroscopy studies[6] suggested that Sb atoms are present in trigonal-bipyramidal geometry, in the present case (in **5** and **6**) the Sb atom is found to favor octahedral geometry.

It has to be mentioned here that a hexa-decanuclear core containing coordination polymer has been reported in very low yields as a byproduct in a reaction involving nickel(II) salts and arylstibonic acid in the presence of NaOMe as base under solvothermal reaction conditions.[9] The structure revealed that the repeat unit consists of aggregates $[(RSb)_{16}O_{28}(OH)_8]$ coordinated to four Na^+ ions. In another recent report, it has been shown that $RSbO_3H_2$ preferentially forms aggregates of the type $[H_8(RSb)_{12}O_{28}]$ when crystallized from NH_3/HOAc.[24] Under basic conditions these aggregates have been shown to act as precursors for formation of isopolyoxostibonates $[Na_2H_9(RSb)_{12}O_{30}]^-$. Despite several attempts to isolate aggregates $[H_8(RSb)_{12}O_{28}]$, polyoxostibonates have been crystallized only in the presence of alkali metal cations such as Na^+ ions. Even when no sodium was used in the reaction, under basic conditions the arylstibonic acid has been reported to form complexes with Na^+ ions from glassware, leading to isolation of alkali metal coordinated isopolyoxostibonates. But in our study, in the presence of mildly basic 3,5-DMPz ligands, aggregates of the type $[(RSb)_{16}O_{28}(OH)_8]$ have been isolated in the absence of any complexing alkali or transition metal ion. This is remarkable since $[(RSb)_{16}O_{28}(OH)_8]$ can be visualized as a naked inorganic cryptand assembled by self-condensation of $RSbO_3H_2$ by elimination of water molecules. Further, parallels to classical POM chemistry need mentioning, as **5** and **6** resemble a type of POM cluster that is rare among otherwise rich structural variations that has been reported. Hexadecanuclear core containing POMs are a rarity, and only a few molybdenum-[25] and vanadium[26]-containing clusters are reported.

Conclusion

In summary, reaction of a phenolic pyrazolyl ligand with arylstibonic acid has led to the isolation of two novel tetranuclear organoantimony oxido clusters. Depending on the steric bulk of the group present on the 5-position of the pyrazole ring, either one or two of the ring N atoms have been found to coordinate to the metal atoms. Remarkably, when 3,5-DMPz is reacted with arylstibonic acids, hexadecanuclear polyoxostibonates have been isolated.

Experimental Section

General Procedures. Solvents, 3,5 DMPz, and common reagents were purchased from commercial sources and used as such. *p*-Halophenylstibonic acids and phenolic pyrazoles were synthesized using literature procedures.[1,27] Infrared spectra were recorded on a JASCO-5300FT-IR spectrometer as KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 instrument. Elemental analysis was performed on a Flash EA Series 1112 CHNS analyzer.

General Synthetic Method. *p*-Halophenylstibonic acid and the ligand were taken in 1:1 stoichiometry in 50 mL of toluene and refluxed for 6 h using a Dean Stark apparatus to remove water eliminated in the reaction as an azeotropic mixture. The clear solution that was obtained was cooled to room temperature, filtered, and evaporated to obtain the crude products. Molar ratios and weights of reactants used are as follows.

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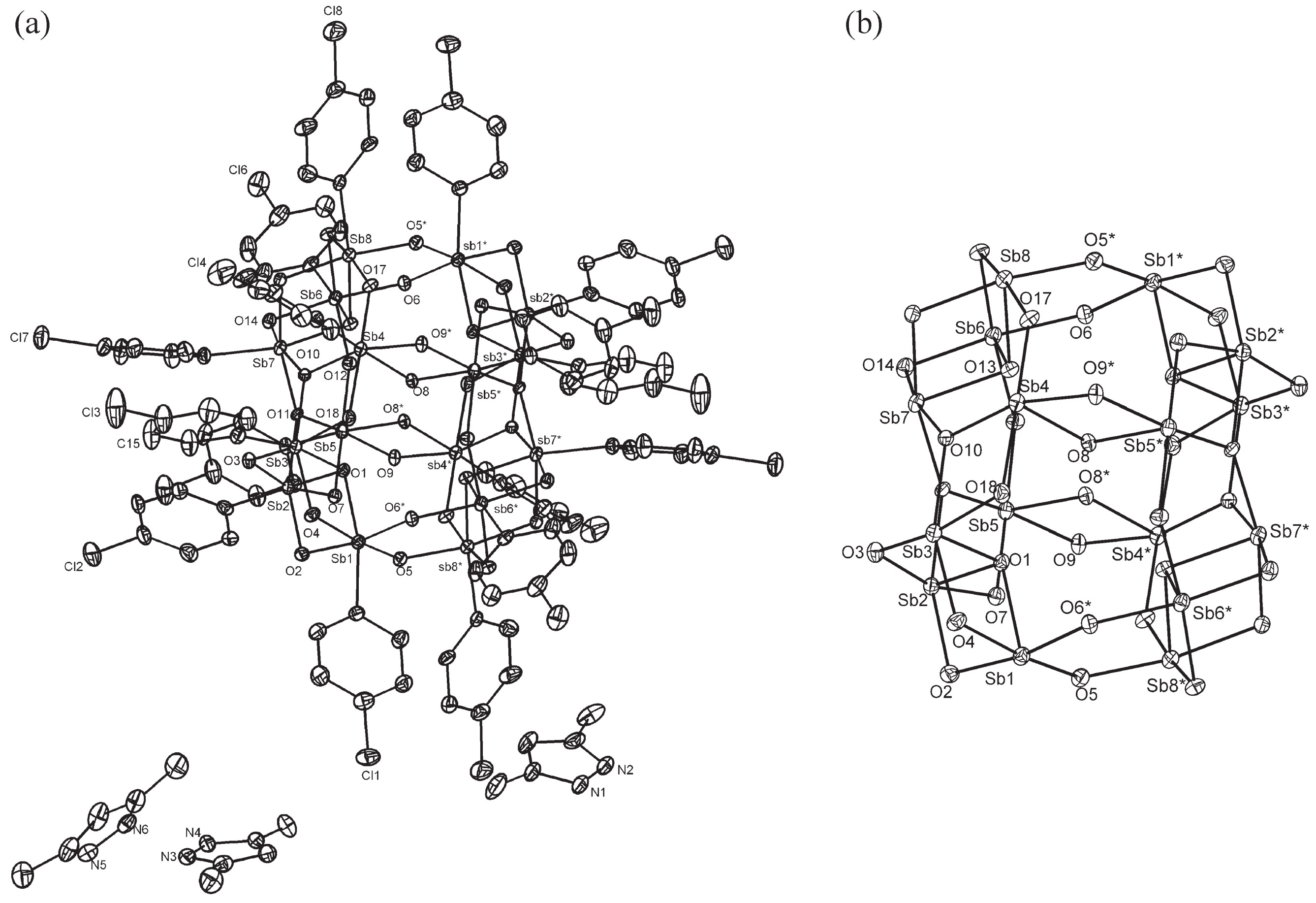

Figure 3. (a) Molecular structure of **5** with thermal ellipsoids shown at 30% probability. (b) Sb−O core of **5**. Selected bond lengths (in Å) and bond angles (in deg): Sb1−O1 = 2.091(6), Sb1−O2 = 2.037(6), Sb1−O4 = 2.023(6), Sb1−O5 = 1.953(6), Sb1−O6 = 1.943(6), Sb2−O1 = 2.084(6), Sb2−O2 = 1.989(6), Sb2−O3 = 1.952(6), Sb2−O7 = 1.953(6), Sb2−O11 = 2.117(6), Sb3−O1 = 2.116(6), Sb3−O3 = 1.953(6), Sb3−O4 = 1.967(6), Sb4−O8 = 2.126(5), Sb4−O10 = 2.094(6), Sb5−O7 = 1.980(6), Sb5−O8 = 2.110(5), Sb5−O9 = 1.961(6), Sb5−O11 = 2.110(5), Sb6−O12 = 1.958(6), Sb6−O14 = 1.984(6), Sb7−O11 = 2.062(5), Sb7−O14 = 1.980(6), Sb8−O15 = 2.042(6), Sb8−O17 = 1.943(6), Sb6−O6* = 1.942(6), Sb4−O17* = 1.931(6), Sb8−O5* = 1.940(6), O5−Sb8* = 1.940(6), O10−Sb3* = 2.149(5), O17−Sb4* = 1.931(6), O2−Sb1−O1 = 77.5(2), O4−Sb1−O1 = 77.6(2), O4−Sb1−O2 = 91.9(2), O6−Sb1−O5 = 95.1(2), O5−Sb1−O4 = 170.9(2), O3−Sb2−O2 = 98.0(2), O7−Sb2−O2 = 93.9(2), O3−Sb2−O1 = 79.8(2), O3−Sb3−O1 = 79.0(2), O18−Sb3−O1 = 91.9(2), O9−Sb4−O8 = 78.1(2), O10−Sb4−O8 = 87.9(2), O9−Sb5−O7 = 91.3(2), O9−Sb5−O8 = 78.4(2), O14−Sb6−O13 = 78.4(2), Sb2−O3−Sb3 = 105.5(3), O14−Sb7−O16 = 93.8(2), O16−Sb8−O15 = 88.7(2), Sb6*−O6-Sb1 = 136.6(3), Sb4*−O17−Sb8 = 136.1(3), O5*−Sb8−O17 = 91.9(2), O17*−Sb4−O10 = 96.7(2), O16−Sb7−O10* = 86.6(2), O11−Sb7−O10* = 90.9(2), O6*−Sb6−O13 = 89.5(2), Sb8*−O5−Sb1 = 136.7(3).

Compound 1: *p*-chlorophenylstibonic acid (0.50 g, 1.76 mmol) and H_2PhPzPh (0.40 g, 1.76 mmol). Colorless crystals of **1** were isolated in a week's time by slow evaporation of toluene. Yield of isolated crystals: 0.42 g (42.80% based on *p*-chlorophenylstibonic acid). Dec temp: 175 °C. Anal. Calcd (%) for $C_{99}H_{74}O_{12}N_{10}Cl_4Sb_4$: C 53.45, H 3.35, N 6.29. Found: C 53.25, H 3.31, N 6.35. IR (cm^{-1}, KBr pellet): 3408 w, 2916 w, 1602 m, 1564 s, 1473 s, 1375 m, 1251 m, 1087 m, 810 s, 758 s, 690 m, 486 m.

Compound 2: *p*-bromophenylstibonic acid (0.50 g, 1.52 mmol) and H_2PhPzPh (0.36 g, 1.52 mmol). Crystals suitable for single-crystal X-ray diffraction were obtained by the diffusion method using $CHCl_3$/hexane in a week's time. Yield: 0.45 g (54.80% based on *p*-bromophenylstibonic acid). Dec temp: 185 °C. Anal. Calcd (%) for $C_{84}H_{62}O_{11}N_8Br_4Sb_4$: C 46.57, H 2.88, N 5.17. Found: C 46.55, H 2.96, N 5.31. IR (cm^{-1}, KBr pellet): 3400 w, 2964 w, 1602 m, 1564 s, 1454 s, 1259 m, 1006 m, 804 s, 758 s, 690 m, 480 m. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95−7.81 ppm (m, 62 H). ^{13}C NMR (100 MHz $CDCl_3$): δ 129.4, 129.2, 129.1, 128.7, 126.6, 125.6, 119.4, 117.1, 116.4 ppm.

Compound 3: *p*-bromophenylstibonic acid (0.50 g, 1.52 mmol) and H_2PhPzt-Bu (0.33 g, 1.52 mmol). Crystals suitable for single-crystal X-ray diffraction were obtained by the diffusion method using CH_2Cl_2/hexane in a week's time. Yield: 0.4 g (50.6% based on *p*-bromophenylstibonic acid). Dec temp: 170 °C. Anal. Calcd (%) for $C_{76}H_{78}O_{11}N_8Br_4Sb_4$: C 43.75, H 3.76, N 5.37. Found: C 43.72, H 3.75, N 5.55. IR (cm^{-1}, KBr pellet): 3271 w, 3065 w, 2962 w, 1602 m, 1558 s, 1475 s, 1381 m, 1257 m, 1116 m, 1087 s, 1064 m, 1037 m, 1012 m, 858 m, 810 m, 756 m, 488 m. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.6−7.6 (m, 40 H), 1.27 ppm (s, 36 H). ^{13}C NMR (100 MHz $CDCl_3$): 148.4, 135.5, 134.7, 130.6, 129.06, 129.2, 126.5, 123.0, 122.8, 119.2, 117.1, 116.9, 31.4, 30.9, 29.7, 28.6, 22.6, 14.17 ppm.

Compound 4: *p*-bromophenylstibonic acid (0.45 g, 1.37 mmol) and H_2PhPz (0.22 g, 1.37 mmol). Colorless crystals were isolated in a week's time by slow evaporation of toluene. Yield: 0.38 g (61.3% based on *p*-bromophenylstibonic acid). Dec temp: 165 °C. Anal. Calcd (%) for $C_{60}H_{40}O_8N_8Br_4Sb_4$: C 39.86, H 2.23, N 6.19. Found: C 40.12, H 2.28, N 6.32. IR (cm^{-1}, KBr pellet): 3124 w, 2964 w, 1602 m, 1602 m, 1564 s, 1485 s, 1358 m, 1261 m, 1228 m, 1082 m, 1006 m, 848 m, 804 s,754 m, 663 m, 480 m.

Compound 5: *p*-chlorophenylstibonic acid (0.45 g, 1.58 mmol) and 3,5 DMPz (0.15 g, 1.58 mmol). Crystals suitable for single-crystal X-ray diffraction were obtained by the diffusion method

Table 1. X-ray Data Collection Parameters for 1−6

	1	**2**	**3**
formula	$C_{113}H_{90}Cl_4N_{10}O_{12}Sb_4$	$C_{87}H_{65}Br_4Cl_9N_8O_{11}Sb_4$	$C_{76}H_{78}Br_4N_8O_{14}Sb_4$
fw, g mol^{-1}	2408.75	2524.16	2134.10
cryst syst	triclinic	triclinic	monoclinic
cryst size, mm	0.34 × 0.20 × 0.18	0.34 × 0.26 × 0.18	0.34 × 0.24 × 0.16
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$
a, Å	14.072(11)	15.639(2)	12.131(3)
b, Å	17.181(14)	17.062(3)	56.572(13)
c, Å	21.742(17)	19.793(3)	14.151(3)
α, deg	93.338(10)	74.305(2)	90
β, deg	105.911(10)	83.621(2)	104.257 (4)
γ, deg	99.635(10)	66.700(2)	90
V, Å^3	4954.2(7)	4669.8(13)	9413(4)
Z	2	2	4
D_{calcd} Mg m^{-3}	1.615	1.795	1.506
T, K	100	100	100
μ, mm^{-1}	1.257	3.175	2.890
F(000)	2412	2456	4184
θ range, deg	1.47 to 26.01	1.42 to 26.06	4.09 to 25.03
index ranges	$-17 \leq h \leq 17$	$-19 \leq h \leq 19$	$-14 \leq h \leq 15$
	$-21 \leq k \leq 21$	$-20 \leq k \leq 21$	$-67 \leq k \leq 67$
	$-26 \leq l \leq 26$	$-24 \leq l \leq 24$	$-16 \leq l \leq 16$
no. of reflns colled	51 784	39 052	84 726
completeness to θ_{max}, %	99.3	98.5	99.2
no. of indep reflns/R_{int}	19 378	18 203	16 501
GooF(F^2)	1.047	1.057	1.075
$R_1(F)$ ($I > 2\sigma(I)$)	0.0351	0.0549	0.0825
$wR_2(F^2)$ (all data)	0.0899	0.1697	0.2004
largest diff peak/hole, e Å^{-3}	2.005/−0.903	2.844/−1.548	1.298/−1.147

	4	**5**	**6**
formula	$C_{88}H_{72}Br_4N_8O_8Sb_4$	$C_{126}H_{120}Cl_{16}N_{12}O_{36}Sb_{16}$	$C_{126}H_{120}Br_{16}N_{12}O_{42}Sb_{16}$
fw, g mol^{-1}	2176.18	4893.54	5700.90
cryst syst	monoclinic	monoclinic	monoclinic
cryst size, mm	0.32 × 0.28 × 0.18	0.38 × 0.28 × 0.22	0.36 × 0.22 × 0.16
space group	$P2(1)/n$	$P2(1)/n$	$P2(1)/n$
a, Å	11.767(8)	18.466(17)	18.548(2)
b, Å	28.368(19)	19.013(17)	19.193(3)
c, Å	24.565(16)	25.074(2)	24.981(3)
α, deg	90	90	90
β, deg	99.242(10)	108.453(10)	108.415(2)
γ, deg	90	90	90
V, Å^3	8093.8(9)	8351.1(13)	8437.4(19)
Z	4	2	2
D_{calcd}, Mg m^{-3}	1.786	1.946	2.244
T, K	100	100	100
μ, mm^{-1}	3.358	2.867	6.377
F(000)	4256	4672	5344
θ range, deg	1.44 to 25.06	1.58 to 25.04	1.37 to 25.14
index ranges	$-13 \leq h \leq 14$	$-21 \leq h \leq 21$	$-21 \leq h \leq 22$
	$-33 \leq k \leq 33$	$-22 \leq k \leq 22$	$-22 \leq k \leq 22$
	$-29 \leq l \leq 29$	$-29 \leq l \leq 29$	$-29 \leq l \leq 29$
no. of reflns colled	77 393	78 209	79 363
completeness to θ_{max} (%)	99.7	99.7	99.1
no. of indep reflns/R_{int}	14 291	14 727	14 952
GooF(F^2)	1.086	1.090	1.050
$R_1(F)$ ($I > 2\sigma(I)$)	0.0258	0.0483	0.0625
$wR_2(F^2)$ (all data)	0.0621	0.1547	0.2012
largest diff peak/hole, e Å^{-3}	0.885/−0.592	2.750/−1.685	4.001/−2.317

using CH_2Cl_2/hexane in a week's time. Yield: 0.20 g (41.2% based on *p*-chlorophenylstibonic acid). Dec temp: 150 °C. Anal. Calcd (%) for $C_{126}H_{120}O_{36}N_{12}Cl_{16}Sb_{16}$: C 30.92, H 2.47, N 3.43. Found: C 31.05, H 2.52, N 3.55. IR (cm^{-1}, KBr pellet): 3202 w, 3136 w, 2928 w, 1574 s, 1475 s, 1381 m, 1298 m, 1261 m, 1089 s, 1066 s, 1012 s, 814 m, 725 m, 488 m. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.9−7.7 (m, 76 H), 1.3 ppm (s, 36 H). ^{13}C NMR (100 MHz $CDCl_3$): δ 143.6, 136.4, 135.4, 134.8, 132.4, 130.8, 128.1, 127.5, 30.3, 29.2, 28.5, 26.7, 22.9, 19.5, 14.05 ppm.

Compound 6: *p*-bromophenylstibonic acid (0.40 g, 1.22 mmol) and 3,5 DMPz (0.12 g, 1.22 mmol). Crystals suitable for single-crystal X-ray diffraction were obtained by the diffusion method using $CHCl_3$/hexane in a week's time. Yield: 0.18 g (42.1% based on *p*-bromophenylstibonic acid)). Dec temp: 165 °C. Anal. Calcd (%) for $C_{126}H_{120}O_{36}N_{12}Br_{16}Sb_{16}$: C 27.00, H 2.15, N 2.99. Found: C 27.45, H 2.26, N 3.11. IR (cm^{-1}, KBr pellet): 3198 w, 3113 w, 2916 w, 1558 s, 1473 s, 1419 m, 1371 m, 1258 m, 1057 m, 1008 s, 808 m, 704 m, 478 m. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.9−7.5 (m, 76 H), 1.28 ppm (s, 36 H). ^{13}C NMR (100 MHz $CDCl_3$): δ 143.7, 135.2, 134.9, 134.3, 131.1, 130.8, 130.0, 124.6, 29.7, 14.14 ppm.

X-ray Crystallography. Single-crystal X-ray data collection for **1**−**6** were carried out at 100(2) 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 and refined using SHELXS-97. Crystals of the compound **3** diffracted weakly at higher angles due to diffused solvated water molecules, and hence a $2\theta = 50°$ cutoff was applied. We were able to model only three solvated water positions at half-occupancies. The remaining solvent contributions were removed by the SQUEEZE[28] command in the Platon program. A disordered bromine atom was freely refined using the FVAR command of the SHELXTL program. The disordered methyl groups of *tert*-butyl units were split into two positions and refined isotropically using similar distance (SADI) and similar *U* restraints (SIMU). The solvated water molecules were refined isotropically, and their hydrogens were not located. Data collection parameters for **1**−**6** are summarized in Table 1. CCDC 750276−750281 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.

Acknowledgment. V.B. thanks the Department of Science and Technology for financial assistance under the SERC−Fast Track Scheme.

Supporting Information Available: ORTEP diagrams of **2**, **3**, and **6** with selected bond lengths and angles are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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