Inorg. Chem. **2002**, *41*, 1652–1657

Inorganic Chemistry
Article

Structures of $Sb(OC_6H_3Me_2\text{-}2,6)_3$ and $Sb(OEt)_5 \cdot NH_3$: The First Authenticated Monomeric $Sb(OR)_n$ ($n = 3, 5$)

Graeme A. Horley, Mary F. Mahon, Kieran C. Molloy,* and Monica M. Venter

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K.

Peter W. Haycock and Christopher P. Myers

Birchall Centre for Inorganic Chemistry and Materials Science, School of Chemistry and Physics,
Lennard−Jones Laboratories, Keele University, Staffordshire ST5 5BG, U.K.

Received June 25, 2001

The first monomeric antimony alkoxides, $Sb(OC_6H_3Me_2)_3$ (**1**) and $Sb(OEt)_5 \cdot NH_3$ (**2**), have been crystallographically characterized. The former adopts a trigonal pyramidal geometry, while the latter is octahedral about antimony; hydrogen bonding between NH_3 and SbOEt groups in $Sb(OEt)_5 \cdot NH_3$ creates a one-dimensional lattice arrangement. Reaction of pyridine with $SbCl_5$ in EtOH/hexane yields the salt $[Hpy^+]_9[Sb_2Cl_{11}^{5-}][Cl^-]_4$ (**3**), which has also been crystallographically characterized. Crystallographic data: **1**, $C_{24}H_{27}O_3Sb$, $a = 10.9080(2)$, $b = 11.9660(2)$, $c = 17.7260(4)$ Å, $\alpha = 109.740(1)°$, monoclinic $P2_1/c$ (unique axis a), $Z = 4$; **2**, $C_{10}H_{28}NO_5Sb$, $a = 7.7220(1)$, $b = 19.0700(2)$, $c = 21.6800(3)$ Å, $\beta = 93.4960(7)°$, monoclinic $P2_1/c$, $Z = 8$; **3**, $C_{45}H_{54}Cl_{15}N_9Sb_2$, $a = 13.4300(2)$, $b = 14.4180(2)$, $c = 17.4180(3)$ Å, $\alpha = 82.7650(7)$, $\beta = 77.5570(7)$, $\gamma = 70.7670(7)°$, triclinic $P\bar{1}$, $Z = 2$.

Introduction

The renaissance of metal alkoxide chemistry, driven over the past decade or more by the material science applications of these species,[1,2] has led to numerous structural studies of these compounds. Homoleptic alkoxides incorporating almost all the elements of the Periodic Table are now known.[3−8] Our interest in this area relates to precursors for the chemical vapor deposition (CVD) of antimony oxide thin films,[9] which have potential applications in a number of areas, including components of electronic ceramics and catalysis.[10−16] The molecular chemistry of volatile antimony precursors, however, appears to have been largely overlooked. Furthermore, with regard to materials chemistry, our recent report on the deposition of Sb_2O_3 and Sb_6O_{13} thin films from commercially available $Sb(OR)_3$ (R = Et, Bu^n)[9] is only matched by a much older work using $SbCl_5$ as a precursor that lacks detailed film characterization.[17]

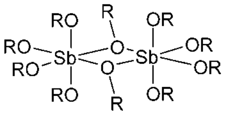
To extend the range of available antimony precursors for future CVD applications, we have prepared a number of Sb(III) and Sb(V) species (β-diketonates, *N*,*N*-dialkylcarbamates) for evaluation. In this paper we focus on antimony alkoxides, which have been known for over half a century[3,18−21] but whose structural chemistry is barren. The only Sb(V) alkoxide that has been crystallographically authenticated is $Sb(OCH_3)_5$, which adopts a dinuclear motif

---

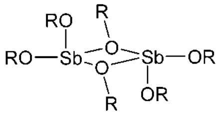
(1) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317.
(2) Bradley, D. C. *Polyhedron* **1994**, *13*, 1111.
(3) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978.
(4) Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269.
(5) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969.
(6) Vandersluys, W. G.; Sattelberger, A. P. *Chem. Rev.* **1990**, *90*, 1027.
(7) Mehrotra, R. C.; Singh, A.; Tripathi, U. M. *Chem. Rev.* **1991**, *91*, 1287.
(8) Mehrotra, R. C.; Singh, A.; Sogani, A. *Chem. Rev.* **1994**, *94*, 1643.
(9) Haycock, P. W.; Horley, G. A.; Molloy, K. C.; Myers, C. P.; Rushworth, S. A.; Smith, L. M. *Chem. Vap. Deposition* **2001**, *7*, 191.
(10) Tianshu, Z.; Hing, P. *J. Mater. Sci.: Mater. Electron.* **1999**, *10*, 509.
(11) Cava, R. J.; Krajewski, J. J.; Qin, Y. L.; Zandbergen, H. W. *J. Mater. Res.* **2000**, *15*, 2672−2676.
(12) Zhang, T. S.; Hing, P.; Zhang, R. F.; Zhang, J. C.; Li, Y. *J. Mater. Res.* **2000**, *15*, 2356.
(13) Brahma, P.; Banerjee, S.; Chakraborty, S.; Chakravorty, D. *J. Appl. Phys.* **2000**, *88*, 6526.
(14) Zhang, Z. L.; Guo, L.; Wang, W. D. *J. Mater. Res.* **2001**, *16*, 803.
(15) Grasselli, R. K.; Burrington, J. D. *Adv. Catal.* **1981**, *30*, 133.
(16) Centi, G.; Perathoner, S. *Appl. Catal.* **1995**, *124A*, 317.
(17) Badawy, W. A.; El-Taher, E. A. *Thin Solid Films* **1988**, *158*, 277.
(18) Maillard, A.; Deluzarche, A.; Maire, J. C.; Havas, L. *Bull. Soc. Chim. Fr.* **1962**, 843.
(19) Maire, J. C.; Havas, L. *C. R. l'Academie. Sci., Ser. II Univers* **1962**, *255*, 2449.
(20) Maillard, A.; Deluzarche, A.; Maire, J. C.; Havas, L. *Bull. Soc. Chim. Fr.* **1965**, 2962.
(21) Athar, T.; Bohra, R.; Mehrotra, R. C. *J. Indian Chem. Soc.* **1990**, *67*, 535.

10.1021/ic0106726 CCC: $22.00

incorporating alkoxide bridges (**I**).[22] Of the two structurally characterized Sb(III) alkoxides, $Sb[OCH(CH_3)_2]_3$ adopts a motif (**II**)[23] that is clearly related to **I**, while $Sb(OCH_3)_3$ forms a layer structure incorporating SbO_6 moieties.[24] Alkoxide bridges are inherent in all these structures and are also a universal feature of related alkoxy-halogenostibanes.[23]



(**I**)



(**II**)

In this paper we report the structures of $Sb(OC_6H_3Me_2\text{-}2,6)_3$ (**1**) and $Sb(OC_2H_5)_5 \cdot NH_3$ (**2**), the first examples of mononuclear Sb(III) and Sb(V) alkoxides in which bridging alkoxides are absent. Also presented is the structure of $[pyH^+]_9[Sb_2Cl_{11}^{5-}][Cl^-]_4$ (**3**; py = C_5H_4N), isolated in attempts to form other amine adducts of $Sb(OEt)_5$.

Experimental Section

General Procedures. Infrared spectra were recorded as Nujol mulls between NaCl plates using a Nicolet 510P FT-IR spectrophotometer; elemental analyses were performed using a Carlo-Erba Strumentazione E.A. model 1106 microanalyzer operating at 500 °C. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX270 FT spectrometer, all using saturated C_6D_6 solutions unless indicated otherwise. $SbCl_5$ and other chemicals purchased from Aldrich and BDH, respectively, were used as supplied as was 2,6-dimethylphenol (Aldrich). All reactions were carried out using previously dried solvents under an argon atmosphere using standard Schlenk techniques.

Synthesis of $Sb(OC_6H_3Me_2\text{-}2,6)_3$ (1). Tris(dimethylamino)-antimony(III) (1.05 g, 4.12 mmol) was transferred to a Schlenk tube in a drybox and diluted with dry hexane (20 mL). 2,6-Dimethylphenol (1.39 g, 12.39 mmol), also diluted in dry hexane (30 mL), was added slowly to the antimony(III) solution, and the resultant clear solution was then allowed to stir overnight. The solvent was removed in vacuo to yield a cream-white solid, which was redissolved in toluene from which colorless crystals were obtained (yield 1.89 g, 84%). Mp: 102−103 °C. Analysis, found (calcd for $C_{24}H_{27}O_3Sb$): C, 57.4 (59.4); H, 5.39 (5.61). ^1H NMR (300 MHz, C_6D_6): 2.35 (s, 18H, CH_3); 6.89 (t, 3H, $p\text{-}C_6H_3$, J = 7.5 Hz); 7.03 (d, 6H, $m\text{-}C_6H_3$, J = 7.5 Hz). ^{13}C NMR (75 MHz, C_6D_6): 18.7 (CH_3); 122.6, 129.7 (C_6H_3); 154.8 (CO). IR (NaCl, cm^{-1}): 1593, 1322, 1263, 1193, 1166, 1088, 1022, 982, 910, 840, 761, 728, 689.

Synthesis of $Sb(OEt)_5 \cdot NH_3$ (2). Antimony(V) chloride (4.45 g, 14.88 mmol) (WARNING: CORROSIVE) was transferred to a round-bottomed two-neck flask and diluted in dry hexane (100 mL). Dry ethanol (15 mL) was then added and the mixture stirred in an ice-cooled water bath. An ammonia cylinder was then attached to the flask, and gas was bubbled slowly through the mixture for ca. 30 min, during which time a white precipitate had been formed. After the ammonia supply was removed, the contents of the flask were allowed to settle at room temperature and the liquid fraction was isolated by cannula filtration. All volatiles were then removed at reduced pressure to give a polycrystalline white powder, which was recrystallized from toluene to give colorless crystals (yield 3.10 g, 57%). Mp: 116−118 °C. Analysis, found (calcd for $C_{10}H_{28}O_5NSb$): C, 31.8 (33.0); H, 7.40 (7.75); N, 3.90 (3.85). ^1H NMR (270 MHz, C_6D_6): 1.13 (t, 9H, CH_3, J = 6.8 Hz); 1.17 (t, 6H, CH_3, J = 6.8 Hz); 3.64 (q, 4H, CH_2, J = 6.9 Hz); 3.88 (q, 6H, CH_2, J = 6.9 Hz). ^{13}C NMR (68 MHz, C_6D_6): 18.4 (CH_3); 18.7 (CH_3); 58.3 (CH_2); 60.3 (CH_2). No resonance was observed for the ammonia protons. IR (NaCl, cm^{-1}): 3160, 1600, 1333, 1157, 1097, 1050, 895, 781, 739.

Synthesis of $[Hpy^+]_9[Sb_2Cl_{11}^{5-}][Cl^-]_4$ (3). Antimony(V) chloride (2.68 g, 8.96 mmol) was transferred to a Schlenk tube and diluted in dry hexane (50 mL). While the mixture was stirred, dry ethanol (4 mL) was slowly added. The $SbCl_5$ was observed to go into the alcohol layer. Then, at room temperature, dry pyridine (4.35 mL, 4.25 g, 53.8 mmol) was slowly added to the mixture. Upon addition of the dry pyridine, a small amount of a yellow oily precipitate was observed and the solution was rather cloudy. The mixture was stirred overnight and then allowed to stand at room temperature for 48 h, by which time clear, needlelike crystals had grown from the light yellow solution. Mp: 113−114 °C dec. Analysis, found (calcd for $C_{45}H_{54}Cl_{15}N_9Sb_2$): C, 34.9 (36.1); H, 4.31 (3.64); N, 6.85 (8.42).

Crystal Structures. All data collections were performed on a Nonius Kappa CCD diffractometer using Mo Kα radiation. Further experimental details relating to the crystallography are given in Table 1.

Colorless crystals of **1** were grown from toluene; an irregular block of dimensions 0.25 × 0.15 × 0.10 mm was used for data collection. Reflections (24 802) were collected in the range $3.62 \leq \theta \leq 28.30°$ of which 5379 were independent ($R_{int} = 0.0709$) and 4305 had $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically. H-Atoms were included at calculated positions. A semiempirical absorption correction was applied (max/min transmission factors: 1.049, 0.960), as were corrections for Lorentz, polarization, and extinction.

Colorless crystals of **2** were grown from toluene; a needlelike crystal of dimensions 0.30 × 0.08 × 0.08 mm was used for data collection. Reflections (92 952) were collected in the range $3.57 \leq \theta \leq 27.46°$ of which 7238 were independent ($R_{int} = 0.0625$) and 6291 had $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically. H-Atoms were included at calculated positions. A multiscan absorption correction was applied (max/min transmission factors: 1.167, 0.939), as were corrections for Lorentz and polarization.

Colorless crystals of **3** were grown directly from the reaction solution (see above); a block of dimensions 0.50 × 0.40 × 0.20 mm was used for data collection. 51 302 reflections were collected in the range $3.62 \leq \theta \leq 27.47°$ of which 14 158 were independent ($R_{int} = 0.0626$) and 9279 had $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically. H-Atoms were included at calculated positions. Corrections for Lorentz, polarization, and extinction were made.

SHELXS-86,[25] SHELXL-97,[26] and ORTEX[27]software was used.

---

[22] Tempel, N.; Schwarz, W.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1981**, *474*, 157.

[23] Fleischer, H.; Bayram, H.; Elzner, S.; Mitzel, N. W. *J. Chem. Soc., Dalton Trans.* **2001**, 373.

[24] Ensinger, U.; Schwarz, W.; Schrutz, B.; Sommer, K.; Schmidt, A. *Z. Anorg. Allg. Chem.* **1987**, *544*, 181.

[25] Sheldrick, G. M. *SHELXS-86*; University of Göttingen: Göttingen, Germany, 1986.

[26] Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

[27] McArdle, P. *J. Appl. Crystallogr.* **1995**, *28*, 65.

Table 1. Crystal Data

	1	**2**	**3**
chemical formula	$C_{24}H_{27}O_3Sb$	$C_{10}H_{28}NO_5Sb$	$C_{45}H_{54}Cl_{15}N_9Sb_2$
fw	485.21	364.08	1496.22
T, K	150(2)	170(2)	150(2)
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (unique axis a)	$P2_1/c$	$P\bar{1}$
a, Å	10.9080(2)	7.7220(1)	13.4300(2)
α (deg)	109.740(1)		82.7650(7)
b, Å	11.9660(2)	19.0700(2)	14.4180(2)
β, (deg)		93.4960(7)	77.5570(7)
c, Å	17.7260(4)	21.6800(3)	17.4180(3)
γ, (deg)			70.7670(7)
volume, Å^3	2177.72(7)	3186.62(7)	3104.14(8)
Z	4	8	2
radiation used, λ (Å)	Mo Kα 0.71070	Mo Kα 0.71070	Mo Kα 0.71070
absorption coefficient, mm^{-1}	1.288	1.741	1.555
density, ρ(calcd) (Mg/m^3)	1.480	1.518	1.601
final R indices [$I > 2\sigma(I)$], R_1, w$R_2(F_o^2)$	0.0335, 0.0872	0.0402, 0.1245	0.0417, 0.1035
R indices (all data), R_1, w$R_2(F_o^2)$	0.0514, 0.0986	0.0495, 0.1341	0.0842, 0.1281

[a] $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

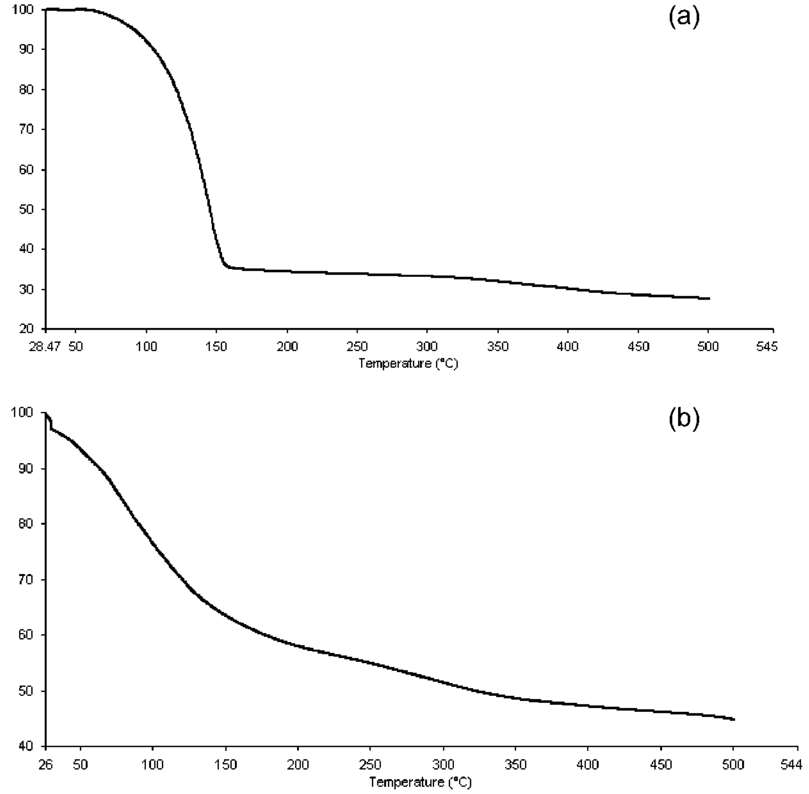


Figure 1. (a) TGA of $Sb(OC_6H_3Me_2\text{-}2,6)_3$ (**1**) and (b) TGA of $Sb(OEt)_5{\cdot}NH_3$ (**2**).

Results and Discussion

$Sb(OC_6H_3Me_2\text{-}2,6)_3$ (**1**) was prepared from the reaction of $2,6\text{-}Me_2C_6H_3OH$ with $Sb(NMe_2)_3$ in hexane, with 84% yield. In the NMR spectra of **1**, a single resonance is observed for the methyl groups indicating their equivalence in all three ligands and a monomeric structure for the complex. Compound **1** is a relatively low-melting solid (102−3 °C) and is soluble in common organic solvents, prerequisites for low-pressure CVD, and aerosol-assisted CVD, respectively. Furthermore, a TGA of **1** (Figure 1a) shows a clean decomposition occurring between ca. 75−150 °C, while the mass of the final residue (500 °C) is close to that required for Sb_2O_3 (found, 27.6; calculated, 30.0%). In separate experiments, **1** was thermally decomposed under nitrogen in a tube furnace at 530 and 625 °C. The resulting powdered solids were shown to be amorphous by X-ray diffraction but were analyzed by qualitative and quantitative EDAX experiments. In both cases, only antimony and oxygen (and the carbon coating to render the samples suitable for EDAX analysis) were detected suggesting that the material was indeed an antimony oxide. The samples were then polished by abrasion to allow a quantitative study. For the product of the 625 °C decomposition, particles had a composition with an atomic ratio of 63.2:36.8 (±1.1)% O:Sb, suggesting a composition close to Sb_2O_3. The sample from the decomposition at 530 °C, however, consistently gave either of two

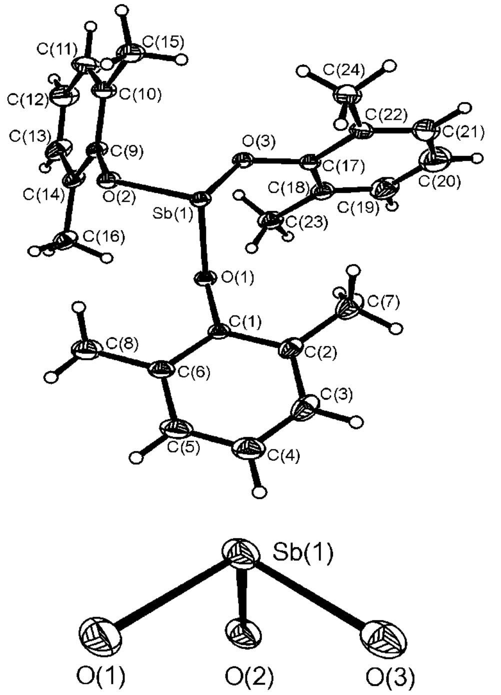


Figure 2. Structure of **1** showing the asymmetric unit and labeling scheme used in the text (top); the pyramidal nature of the antimony coordination sphere is also highlighted (bottom). Thermal ellipsoids are at the 30% level. Selected metrical data: Sb(1)−O(1) 1.976(2) Å, Sb(1)−O(2) 1.967(2) Å, Sb(1)−O(3) 1.968(2) Å; O(1)−Sb(1)−O(2) 95.00(9)°, O(2)−Sb(1)−O(3) 89.75(8)°, O(1)−Sb(1)−O(3) 93.76(8)°, C(1)−O(1)−Sb(1) 119.9(2)°, C(17)−O(3)−Sb(1) 125.7(2)°, C(9)−O(2)−Sb(1) 128.8(2)°.

results, suggesting the sample to be heterogeneous. A relatively dark and sticky material gave an O:Sb ratio of 54.9: 45.1 (±1.3)%, but with the added detail that these two elements only made up on average ca. 91% of the molar content of the material as a whole. This might suggest incomplete decomposition of **1** to the oxide. A slightly lighter colored fraction of the sample gave a ratio of 60.0:40.0 (±1.8)% O:Sb ratio consistent with the formation of Sb_2O_3.

Crystals of **1** were grown from toluene. Compound **1** is isostructural with $Bi(OC_6H_3Me_2\text{-}2,6)_3$,[28] adopting a trigonal pyramidal architecture capped by a stereochemically active lone electron pair (Figure 2). The Sb−O bonds [1.967(2)−1.976(2) Å] are similar to the analogous distances in $Sb(OPr^i)_3$, which weakly dimerizes to raise the coordination number (CN) at Sb to 4 [1.935(2)−1.976(2) Å],[23] but shorter than those in $Sb(OMe)_3$, where the CN at antimony is 6 [1.986(6)−2.102(8) Å].[24] Moreover, the Sb−O bonds in **1** are also longer than those calculated for monomeric $Sb(OMe)_3$ [1.958 Å],[23] which reflects the steric congestion about the basal plane of the trigonal pyramid. Although the Sb−O bonds are shorter than the Bi−O bonds in $Bi(OC_6H_3Me_2\text{-}2,6)_3$ [av 2.091(5) Å], the O−Sb−O [89.75(8)−95.00(9)°] and Sb−O−C [119.9(2)−128.8(2)°] angles are comparable with the equivalent angles in the latter [av 92(2), 123(4)°, respectively].[28]

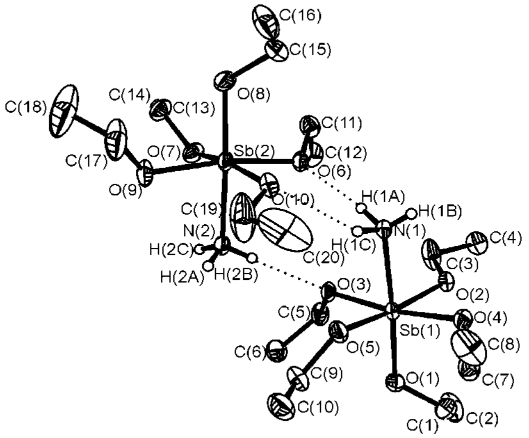


Figure 3. Structure of **2** showing the labeling scheme used in the text; thermal ellipsoids are at the 30% level. Selected metrical data: Sb(1)−O(1) 1.950(3) Å, Sb(1)−O(2) 1.975(3) Å, Sb(1)−O(3) 1.975(3) Å, Sb(1)−O(4) 1.969(3) Å, Sb(1)−O(5) 1.960(3) Å, Sb(1)−N(1) 2.145(4) Å, Sb(2)−O(6) 1.967(3) Å, Sb(2)−O(7) 1.957(3) Å, Sb(2)−O(8) 1.945(3) Å, Sb(2)−O(9) 1.975(3) Å, Sb(2)−O(10) 1.970(3) Å, Sb(2)−N(2) 2.158(4) Å; O(2)−Sb(1)−O(5) 169.2(1)°, O(3)−Sb(1)−O(4) 171.0(1)°, O(1)−Sb(1)−N(1) 176.6(1)°, O(7)−Sb(2)−O(10) 168.9(1)°, O(6)−Sb(2)−O(9) 171.6(2)°, O(8)−Sb(2)−N(2) 177.3(1)°.

$Sb(OEt)_5{\cdot}NH_3$ (**2**) was prepared by the method of Mehrotra by passing NH_3 through a mixture of $SbCl_5$ and EtOH.[21] The ethoxy groups are nonequivalent in solution, while IR confirms the incorporation of ammonia by a strong broad band centered on 3160 cm^{-1} due to ν(NH). Like compound **1**, **2** is relatively low-melting (116−118 °C) and is soluble in common organic solvents. Its decomposition profile (Figure 1b), however, shows a continuous decrease in weight between room temperature and 650 °C, though the majority of the mass is lost by ca. 300 °C; this indicates that **2** is unlikely to be a suitable CVD precursor. A trial CVD run at low pressure heating the sample at 200 °C showed no deposition onto a glass substrate heated separately to 550 °C; a pale brown residue remained in the sample boat at the end of the experiment (C, 4.03; H, 1.66; N, 1.55). The low volatility and indistinct decomposition pathway are likely to result from the network of hydrogen bonds evident in the crystal lattice (see below).

Crystals suitable for X-ray crystallography were grown from toluene; hydrogen atoms were located in the difference map but were refined at fixed distances from their parent atom. The structure of **2** is shown in Figure 3; the asymmetric unit consists of two molecules. Each antimony is octahedrally coordinated in an SbO_5N environment. Molecules arrange themselves in chains held together by N−H···O−C hydrogen bonds involving all three hydrogen atoms on each ammonia. Any pair of molecules is held by three hydrogen bonds, i.e., N(1)−H(1A)···O(6) 1.98, N(1)−H(1C)···O(10) 2.46, and N(2)−H(2B)···O(3) 2.08 Å or N(2)−H(2A)···O(4′) 2.29, N(2)−H(2C)···O(2′) 2.09, and N(1)−H(1B)···O(9′) 2.15 Å. Of these, only N(2)−H(2C)···O(2′) approaches linearity (171.3°), the other interactions subtending angles at hydrogen in the range 119.8−160.7° (Table 2). Individual hydrogen bonds are thus weak, and the lattice organization relies on the cumulative effect of the hydrogen bond collective.

The involvement of the alkoxide groups in hydrogen bonding does, however, manifest itself in the Sb−O bonds. The shortest Sb−O bond is formed by a non-hydrogen

---

[28] Evans, W. J.; Hain, J. H. J.; Ziller, J. W. *J. Chem. Soc., Chem. Commun.* **1989**, 1628.

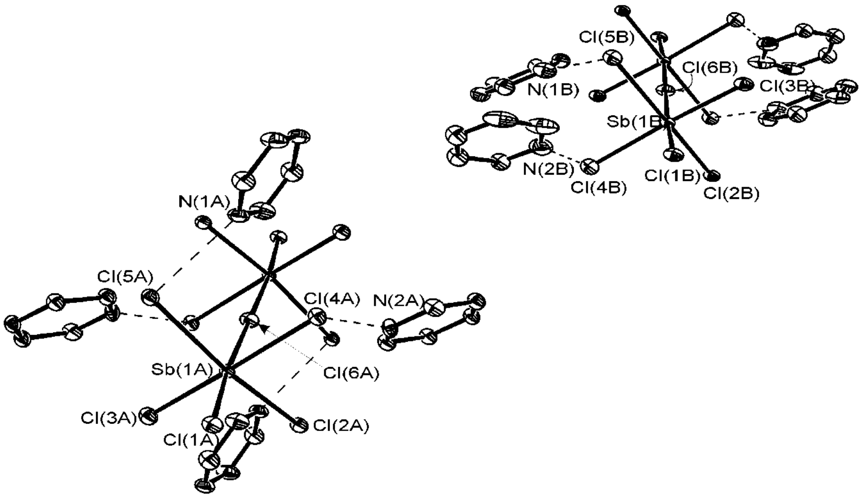


Figure 4. Structure of **3** showing the labeling scheme used in the text; thermal ellipsoids are at the 30% level. Four units of $[Hpy]^+[Cl]^-$ not associated with each of the two $Sb_2Cl_{11}^{5-}$ moieties in the asymmetric unit have been excluded for clarity. Selected metrical data: Sb(1A)−Cl(1A) 2.489(1) Å, Sb(1A)−Cl(2A) 2.502(1) Å, Sb(1A)−Cl(3A) 2.548(1) Å, Sb(1A)−Cl(4A) 2.774(1) Å, Sb(1A)−Cl(5A) 2.897(1) Å, Sb(1A)−Cl(6A) 2.867(2) Å, Sb(1B)−Cl(1B) 2.483(1) Å, Sb(1B)−Cl(2B) 2.453(1) Å, Sb(1B)−Cl(3B) 2.548(1) Å, Sb(1B)−Cl(4B) 2.740(1) Å, Sb(1B)−Cl(5B) 3.012(2) Å, Sb(1B)−Cl(6B) 2.9921(3) Å; Cl(1A)−Sb(1A)−Cl(6A) 175.67(3)°, Cl(2A)−Sb(1A)−Cl(5A) 173.12(3)°, Cl(3A)−Sb(1A)−Cl(4A) 175.63(3)°, Sb(1A)1−Cl(6A)−Sb(1A′) 180.0°, Cl(1B)−Sb(1B)−Cl(6B) 176.69(2)°, Cl(2B)−Sb(1B)−Cl(5B) 174.28(4)°, Cl(3B)−Sb(1B)−Cl(4B) 175.54(4)°, Sb(1B)1−Cl(6B)−Sb(1B′) 180.0°.

Table 2. Hydrogen Bonding in **2**

D−H[a]	A	*d*(H−O) (Å)	<N−H···O angle (deg)	*d*(N···O) (Å)
N1−H1A	O6	1.98	160.7	2.859
N1−H1B	O9[b]	2.15	146.0	2.945
N1−H1C	O10	2.46	119.8	3.015
N2−H2A	O4[c]	2.29	129.6	2.951
N2−H2B	O3	2.08	171.3	2.985
N2−H2C	O2[c]	2.09	150.9	2.916

[a] *d*(N−H) = 0.910 Å. [b] *x*+1, *y*, *z*. [c] *x* − 1, *y*, *z*.

bonding alkoxide *trans* to the coordinated NH_3 [Sb(1)−O(1) 1.950(3) Å; Sb(2)−O(8) 1.945(3) Å], followed by the bond formed between the metal and the only other non-hydrogen bonding alkoxide [Sb(1)−O(5) 1.960(3) Å; Sb(2)−O(7) 1.957(3) Å]. Sb−O distances involving the remaining alkoxides, all of which participate in hydrogen bonding, are longer [1.967(3)−1.975(3) Å], though the weakness of the associated hydrogen bonds leaves the bond lengthening at the margins of experimental error.

Comparative data for the N:→Sb bond are relatively scarce, particularly when donors that are a part of cyclic systems (and hence subject to constraints of bite-angle) are excluded. Suitable comparisons can be made with the donor N:→Sb bond in $[ClSb(HNMe_2)(\mu\text{-}NBu^t)]_2$ [2.524(3) Å][29] and $[Cl_2Sb(HNMe_2)(\mu\text{-}OEt)]_2$ [2.402(5) Å],[29] against which the coordinated ammonia in **2** is extremely strongly bound [Sn(1)−N(1) 2.145(4) Å; Sb(2)−N(2) 2.158(4) Å]. Indeed, the bond length approaches that of covalent, terminally bound amido groups, e.g., $[Me_2NSb(\mu\text{-}NC_6H_3Pr^i{}_2\text{-}2,6)]_2$ 1.983(8) Å[30] and $[Me_2NSb(\mu\text{-}NC_6H_2(OMe)_3\text{-}3,4,5)]_2$ 2.013(5) Å.[31]

In an attempt to synthesize $Sb(OR)_5{\cdot}L$ adducts excluding hydrogen bonding, pyridine was added to $SbCl_5$ in an ethanol/hexane mixture. Needle-shaped crystals of $[Hpy^+]_9[Sb_2Cl_{11}^{5-}][Cl^-]_4$ (**3**) were the only identifiable product isolated. The compound is air sensitive and precluded an accurate microanalysis, though its nature has been determined unambiguously by an X-ray structure (Figure 4). The formation of the product requires both HCl formation (implying also the generation of Sb−OR moieties) and reduction of Sb(V) to Sb(III). At the center of the structure is the centrosymmetric Sb(III) anion $Sb_2Cl_{11}^{5-}$ in which $SbCl_5$ units are linked by a linear Sb−Cl−Sb bridge [Sb(1)−Cl(6)−Sb(1′), 180.0°]. The overall structure of **3** consists of two centrosymmetric, dinuclear complex anions $[Sb_2Cl_{11}^{5-}]$ (indicated as A and B, Figure 3), eighteen Hpy^+ cations, and eight uncoordinated Cl^- species. Each $Sb_2Cl_{11}^{5-}$ anion contains two Sb(III) centers, the octahedral $SbCl_5$ units being linked by linear Sb−Cl−Sb bridges [Sb(1)−Cl(6) 2.8666(2), 2.9921(3) Å for A, B, respectively]. This anion has only been structurally characterized on one other occasion, $[H_3NCH_2CH_2NH_3^+]_5[Sb_2Cl_{11}^{5-}]{\cdot}4H_2O$,[32] though the Sb_2Cl_{11} subunit appears within the more complex anions $[Sb_4Cl_{20}^{8-}]$[33] and $[Sb_4Cl_{18}^{6-}]$.[34,35] The structure of the $Sb_2Cl_{11}^{5-}$ anions in **3** shows no unusual features when compared to the literature data, all Sb−Cl bond lengths [2.453(1)−3.012(1) Å] falling in the range of the corresponding distances found for related compounds [cf. $[Hpy]_3[Sb_2Cl_9]$ 2.394(2)−3.093(3) Å].[35] Of the Hpy^+ cations, eight are linked to either Cl(5) or Cl(4) atoms of the $Sb_2Cl_{11}^{5-}$ anions through weak N−H···Cl hydrogen bonds, while the remaining Hpy^+ moieties display similar interactions with the uncoordinated Cl^- anions. All N···Cl and H···Cl distances of **3** described by these contacts [N···Cl, 3.05−3.30; H···Cl, 2.18−2.60 Å] are consistent with

---

(29) Edwards, A. J.; Leadbeater, N. E.; Paver, M. A.; Raithby, P. R.; Russell, C. A.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1994**, 1479.

(30) Beswick, M. A.; Harmer, C. N.; Hopkins, A. D.; Paver, M. A.; Raithby, P. R.; Wright, D. S. *Polyhedron* **1998**, *17*, 745.

(31) Edwards, A. J.; Paver, M. A.; Rennie, M.-A.; Raithby, P. R.; Russell, C. A.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1994**, 2963.

(32) Chaabouni, S.; Kamoun, S.; Daoud, A.; Jouini, T. *J. Chem. Cryst.* **1997**, *27*, 401.

(33) Lipka, A. *Z. Naturforsch., B: Chem. Sci.* **1983**, *38*, 1615.

(34) Kallel, A.; Bats, J. W. *Acta Crystallogr., Sect. C* **1985**, *41*, 1022.

(35) Hall, M.; Nunn, M.; Begley, M. J.; Sowerby, D. B. *J. Chem. Soc., Dalton Trans.* **1986**, 1231.

those found for $[Hpy]_3[Sb_2Cl_9]$ [N···Cl, 3.23−3.36; H···Cl, 2.31−2.36 Å].[35]

Conclusions

Monomeric $Sb(OR)_n$ ($n = 3, 5$) have been structurally characterized for the first time in the form of $Sb(OC_6H_3Me_2\text{-}2,6)_3$ and $Sb(OEt)_5 \cdot NH_3$. The former is pyramidal, while the latter is octahedral at antimony. Reaction of $SbCl_5$ and ethanol in the presence of pyridine yielded $[Hpy^+]_9[Sb_2Cl_{11}{}^{5-}][Cl^-]_4$ and not the expected adduct $Sb(OEt)_5 \cdot py$.

Acknowledgment. This work was supported financially by the EPSRC, NATO, and the Royal Society. JREI and EPSRC are also thanked for funding the purchase of the diffractometer.

Supporting Information Available: Three X-ray Crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0106726