Dinuclear and Tetranuclear Cages of Oxodiphenylantimony Phosphinates: Synthesis and Structures

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The novel dimeric compounds $[Ph_2Sb(O_2PR_2)O]_2 \cdot 2CH_2Cl_2$ [R = cycl-C_6H_{11} (**2**) and cycl-C_8H_{15} (**3**)] have been synthesized by reacting diphenylantimony trichloride (**1**) with 3 mol equiv of silver acetate followed by 1 mol equiv of the phosphinic acid. By the same route under more stringent conditions to exclude moisture, the mixed phosphinate−acetate $[Ph_2Sb(O_2P(C_6H_{11})_2)(O_2CMe)]_2O$ (**4**) was isolated and characterized. Treatment of **2** with acetic acid/water affords the tetranuclear cage $Ph_8Sb_4O_4(OH)_2(O_2P(C_6H_{11})_2)_2 \cdot CH_3COOH \cdot CH_2Cl_2$ (**5**); it is possible to convert **5** to **2** by heating it with an excess of the phosphinic acid. Compounds **2**, **3**, and **5** have been characterized by X-ray structural analysis. All of them possess four membered Sb_2O_2 rings with hexacoordinated antimony. In **5** the antimony atoms in the two Sb_2O_2 rings are connected by oxo bridges on two sides to give an Sb_4O_6 cage. These structures are correlated with those of known tin cages.

Introduction

Recently, we have reported the synthesis and structures of two oxo-bridged antimony(V) compounds $[Ph_2SbCl(O_2P(C_6H_{11})_2)]_2O$ (**I**) and $[Ph_2Sb(O_2CPh)_2]_2O$ (**II**) in which the

(I)   (II)
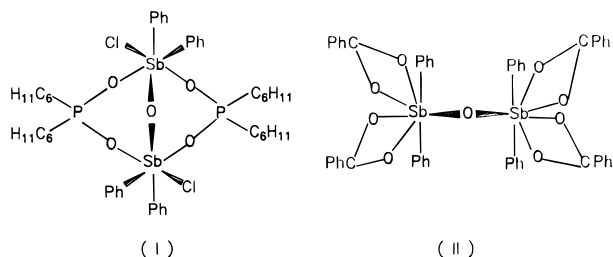
antimony exhibits coordination numbers of 6 and 7, respectively.[1] In the course of the reactions leading to **I** or its dicyclooctyl phosphinate analogue $[Ph_2SbCl(O_2P(C_8H_{15})_2)]_2O$, ^{31}P NMR analysis showed the formation of other products. Coupled with this observation, the possibility of replacement of the carboxylates in **II** and in the corresponding acetate $[Ph_2Sb(O_2CMe_2)]_2O$[2] by phosphinates to generate new cages prompted us to probe these reactions further. Analogous replacement reactions on the prismane $[MeSnO \cdot O_2CMe]_6$ in tin chemistry led to the novel "mixed prismane" $[MeSnO \cdot ^1/_2O_2-CMe \cdot ^1/_2O_2P(t\text{-}bu)_2]_6$[3] and "crown" $[(MeSn(O)O_2P(t\text{-}bu)_2)(MeSn-(OH)(OMe)(O_2P(t\text{-}bu)_2))]_2[H][O_2P(t\text{-}bu)_2] \cdot 4MeOH \cdot 2H_2O$.[4] As both tin and antimony in their respective higher oxidation states

of +4 and +5 can be expected to achieve coordination numbers of 6 and 7 readily, structural analogies and related chemistry can be envisioned for them. Thus we report herein the synthesis and X-ray structures of three oxoantimony(V) phosphinate compounds, $[Ph_2Sb(O_2PR_2)O]_2$ [R = cycl-C_6H_{11} (**2**), cycl-C_8H_{15} (**3**)] and $Ph_8Sb_4O_4(OH)_2(O_2P(C_6H_{11})_2)_2 \cdot CH_3COOH \cdot CH_2Cl_2$ (**5**); the structures of these derivatives have been correlated with those of the analogous tin compounds. The structural interconversion between the dinuclear and the tetranuclear cages **2** and **5** is also described.

Experimental Section

Chemicals were produced from Aldrich/Fluka or from local manufacturers; they were purified when required. Diphenylantimony trichloride was prepared according to a literature procedure.[5] Solvents were purified according to standard procedures.[6] Silver salts of phosphinic acids were prepared by treating the acid with a stoichiometry quantity of aqueous sodium hydroxide followed by aqueous silver nitrate, washing the precipitate with methanol, and drying *in vacuo*. All reactions, unless stated otherwise, were performed under dry nitrogen atmosphere. ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker 200 MHz spectrometer in CDCl$_3$ solutions with shifts referenced to SiMe$_4$ (δ = 0) or 85% H$_3$PO$_4$ (δ = 0) IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyzer.

CAUTION! Toxicity of the antimony compounds reported here is unknown, and hence all of them should be handled with care.

Dimeric Oxodiphenylantimony Dicyclohexylphosphinate, [Ph$_2$-Sb(O$_2$P(C$_6$H$_{11}$)$_2$)O]$_2$·2CH$_2$Cl$_2$ (2). Route (A). A mixture of diphenylantimony trichloride (**1**) (1.01 g, 2.66 mmol) and silver acetate (1.77 g, 0.63 mmol) was heated in dry toluene (50 mL) for 3 h under reflux and then filtered. The precipitate was washed with 10 mL of dry toluene, and the washings were added to the filtrate. To this filtrate dicyclohexylphosphinic acid[7] (1.2 g, 2.66 mmol) was added and the mixture heated overnight under reflux. The ^{31}P NMR spectrum of the

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Table 1. Crystal Data for **2**, **3**, and **5**

	2	**3**	**5**
empirical formula	$C_{50}H_{68}Cl_4O_6P_2Sb_2$	$C_{29}H_{42}Cl_2O_3PSb$	$C_{75}H_{92}Cl_2O_{12}P_2Sb_4$
fw	1212.28	662.28	1805.43
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/a$	$P2_1/n$
Z	1	4	4
a/Å	10.520(12)	12.119(2)	15.111(2)
b/Å	11.609(10)	19.739(3)	27.860(5)
c/Å	13.35(2)	13.155(2)	18.669(2)
α/deg	64.65(8)		
β/deg	71.86(9)	112.21(1)	101.10(1)
γ/deg	68.70(8)		
V/Å^3	1350(3)	2913.4(8)	7712(1)
D_c/(g cm^{-3})	1.492	1.510	1.555
cryst size/mm	0.2 × 0.2 × 0.4	0.4 × 0.2 × 2	0.3 × 0.2 × 0.1
$F(000)$	616	1360	3624
μ(Mo Kα)/cm^{-1}	13.03	12.19	15.52
T/°C	20	−110	23
scan method	$\omega - \theta$	$\omega - 2\theta$	$\omega - 2\theta$
2θ range/deg	3.44−34.88	50.1 (max)	50.1 (max)
total reflcns	1713	5615	14492
unique reflcns	1713	5349	13936
obsd reflcns	1673 ($I > 2\sigma(I)$)	4372 ($I > 3\sigma(I)$)	4637 ($I > 3\sigma(I)$)
diffractom used	Siemens stoe AED2	Rigaku AFC5R	Rigaku AFC5R
final R indices	$R_1 = 0.0335$ ($I > 2\sigma(I)$)	$R^a = 0.028$ ($I > 3\sigma(I)$)	$R^a = 0.061$
	$WR_2 = 0.0836$	$R_w{}^a = 0.037$	$R_W{}^a = 0.053$
largest diff.: peak; hole	0.474; −0.434	0.94; −0.68	1.26; −0.73

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|^2/\sum wF_o^2\}^{1/2}$.

reaction mixture showed a major peak at 64.3 ppm (>70%) and two minor peaks at 61.1 and 54.2 ppm. The solvent was completely removed from the mixture and the residue crystallized from dichloromethane−hexane (1:3). Yield: 1.5 g, 54% (mp 284 °C). IR (major bands): 1043 (ν(P=O)) and 962 cm^{-1}. ^{1}H-NMR (after powdering and drying in vacuum): δ 0.70−2.20 (br m, 44H, C$_6H_{11}$), 7.20−8.00 (m, 20H, H(Ar)). [If no evacuation is done, a peak at 5.3 ppm for dichloromethane solvate is observed.] ^{31}P NMR: δ 64.3. Anal. Calcd for $C_{49}H_{66}Cl_2O_2P_2Sb_2$: C, 52.20; H, 5.86. Found: C, 51.34; H, 5.81.

Route (B). A mixture of **1** (0.39 g, 1.06 mmol) and AgO$_2$P(C$_6H_{11}$)$_2$ (2.65 g, 7.87 mmol) was heated under reflux in dry toluene (60 mL) for 24 h and filtered. The solvent was removed from the filtrate and the residue crystallized from dichloromethane−hexane in air to obtain **2**. Yield: 0.44 g, 40%. Mp, IR, and ^{31}P NMR of the crystalline product were identical to that obtained by route A.

Dimeric Oxodiphenylantimony Dicyclohexylphosphinate, [Ph$_2$-Sb(O$_2$P(C$_8H_{15}$)$_2$)O]$_2$·2CH$_2$Cl$_2$ (3). The procedure was similar to that for **2** (routes A or B). Route (A): The following quantites were used: **1**, 1.97 g, 5.17 mmol; silver acetate, 2.5 g, 15.50 mmol; dicyclooctylphosphinic acid (mp 118 °C; ^{31}P NMR, 66.7 ppm; procedure for preparation similar to that for dicyclohexylphosphinic acid[7]) 2.96 g, 10.33 mmol. The ^{31}P NMR spectrum of the reaction mixture shows a major peak at 69.6 ppm (>70%) and two minor peaks at 66.1 and 60.5 ppm. The product was crystallized from dichloromethane−hexane. Yield: 2.3 g, 38.6% (mp 255 °C). IR (major bands): 1039 (ν(P=O)) and 960 cm^{-1}. ^{1}H NMR (after drying): δ 0.90−2.30 (br m, 60H, C$_8H_{15}$), 7.08−7.95 (m, 20H, H(Ar)). [A peak for dichloromethane solvent is observed at 5.3 ppm if the sample is not dried.] ^{31}P NMR 69.6. Anal. Calcd for $C_{56}H_{80}O_6P_2Sb_2$ (after drying): C, 58.26; H, 6.94. Found: C, 57.75; H, 7.08. The same compound could be obtained from route B in 40% yield.

(μ-Oxo)bis[diphenylantimony dicyclohexylphosphinate acetate], [Ph$_2$Sb(O$_2$P(C$_6H_{11}$)$_2$)(O$_2$CMe)]$_2$O (4). A mixture of **1** (0.50 g, 1.31 mmol) and silver acetate (0.875 g, 5.25 mmol) was heated in dry toluene (20 mL) for 3 h under reflux and filtered. To the filtrate, dicyclohexylphosphinic acid (0.30 g, 1.31 mmol) was added and the mixture heated under reflux for 5 h. Then the solvent was removed and the residue crystallized from dichloromethane−heptane (1:7) with stringent precautious against the ingress of moisture. Yield: 0.40 g, 27% (mp 218 °C). IR (major bands only): 1680 (ν(C=O)), 1278, 1091 (ν(P=O)), 1014, and 981 cm^{-1}. ^{1}H NMR (after drying): δ 0.70−2.00 (br m, 44H, C$_6H_{11}$), 2.05 (s, 6H, CH_3), 7.23−8.15 (m, 20H, H(Ar)). ^{31}P NMR: δ 53.3 Anal. Calcd for $C_{52}H_{70}O_9P_2Sb_2$: C, 54.60; H, 6.12. Found: C, 54.10; H, 6.23.

Compound **4** is moisture sensitive and gives either **2** or **5** upon hydrolysis; thus crystals of **5** suitable for X-ray were grown while an attempt was made to crystallized **4** from dichloromethane−hexane mixture.

Tetrameric cage Ph$_8$Sb$_4$O$_4$(OH)$_2$(O$_2$P(C$_6H_{11}$)$_2$)$_2$·HO$_2$CMe·CH$_2$Cl$_2$ (5). A mixture of dimer **2** (0.50 g, 0.48 mmol), acetic acid (3 mL), and water (0.2 mL) was heated under reflux for 2 h. Acetic acid was removed, and the compound was crystallized from dichloromethane−hexane (1:5). Yield: 0.60 g, 69% (mp 248 °C). IR (major bands only): 1761, 1705 (ν(C=O)) and 1072 (ν(P=O)) cm^{-1}. ^{1}H NMR (after evacuation and removal of solvate): δ 0.63−2.15 (br m, 44H + 3H, C$_6H_{11}$ + CH$_3$), 3.50−3.90 (br, 2H, OH), 6.97−8.00 (m, 40H, H(Ar)). One solvent molecule (CH$_2$Cl$_2$; δ(^{1}H) 5.2 ppm) per tetrameric cage is observed if no evacuation is performed. ^{31}P NMR: δ 57.7. Anal. Calcd for $C_{74}H_{90}O_{12}P_2Sb_4$: C, 51.69; H, 5.28. Found: C, 51.45; H, 5.05.

Conversion of the Tetrameric Cage (5) to the Dimer (2). A mixture of **5** (0.05 g) and dicyclohexylphosphinic acid (0.02 g) was heated under reflux in toluene (7 mL) with azeotropic removal of water for 12 h. The solvent was completely removed and ^{31}P NMR recorded for the mixture; it showed compound **2** [δ(^{31}P): 64.2 ppm (>85%)]. Two other minor products [δ(^{31}P): 53.8 (<5%), 45.9 (<5%)] and the excess of the phosphinic acid were also present, at 64.3 (major, >85%, compound **2**), 59.9 (phosphinic acid), 53.8 (<5%), and 45.9 (<5%) ppm.

X-ray Crystallography. Single crystals of compounds **2** and **3** for X-ray crystallography were grown from a mixture of dichloromethane and hexane; compound **5** (for X-ray work) was initially obtained while an attempt was made to recrystallize **4**, and hence the solvent mixture of dichloromethane and hexane contained traces of acetic acid. A suitable crystal was mounted on a glass fiber [for **3** and **5**] or inside a Lindemann capillary (for **2**). Data were collected on a Siemens Stoe AED2 or Rigaku AFC5R diffractometer with graphite monochromated Mo Kα radiation. Three control reflections, collected every 150 reflections, showed no significant changes in intensities for **3** and **5**; however, for **2** the intensities dropped very quickly, and hence, data was collected only up to 2θ of 35 °C. The details pertaining to data collection and refinement are listed in Table 1. The structures were solved by conventional methods[8,9] and refined by the full-matrix least squares method.[9] An empirical absorption correction was applied, and the data were corrected for Lorentz and polarization effects. Neutral atom scattering factors and anamolous-scattering correction terms were taken from *International Tables for X-ray crystallography*. The final positional parameters are listed in Tables 2−4. For compound **2**, the Sb, P, O, and Cl atoms were refined anisotropically, while for **3** all
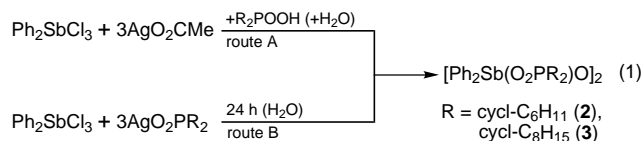
Table 2. Positional Parameters for **2**

atom	x	y	z
Sb	0.1267 (1)	−0.1114 (1)	0.4865 (1)
P	0.1778 (2)	0.1633 (3)	0.4558 (2)
O(1)	0.0053 (5)	0.0492 (4)	0.3926 (4)
O(2)	0.0201 (5)	0.2101 (4)	0.4897 (4)
O(3)	0.2393 (5)	0.0167 (5)	0.4862 (4)
C(1)	0.2392 (8)	−0.1512 (7)	0.3352 (6)
C(2)	0.3348 (9)	−0.0842 (9)	0.2615 (7)
C(3)	0.3987 (10)	−0.1015 (10)	0.1574 (9)
C(4)	0.3614 (10)	−0.1828 (9)	0.1286 (8)
C(5)	0.2702 (9)	−0.2506 (9)	0.1998 (8)
C(6)	0.2079 (9)	−0.2371 (8)	0.3059 (7)
C(7)	0.2404 (8)	−0.2767 (7)	0.6051 (6)
C(8)	0.1771 (10)	−0.3212 (9)	0.7167 (7)
C(9)	0.2506 (10)	−0.4324 (10)	0.7950 (9)
C(10)	0.3854 (10)	−0.4956 (9)	0.7587 (8)
C(11)	0.4464 (10)	−0.4539 (9)	0.6504 (8)
C(12)	0.3747 (9)	−0.3426 (8)	0.5705 (7)
C(13)	0.2276 (8)	0.2568 (7)	0.3098 (6)
C(14)	0.1516 (9)	0.4030 (8)	0.2693 (7)
C(15)	0.1912 (10)	0.4668 (10)	0.1403 (8)
C(16)	0.3446 (10)	0.4447 (9)	0.1023 (8)
C(17)	0.4235 (10)	0.3020 (9)	0.1430 (8)
C(18)	0.3855 (9)	0.2375 (9)	0.2724 (7)
C(19)	0.2514 (9)	0.1903 (7)	0.5466 (6)
C(20)	0.1947 (10)	0.3332 (9)	0.5442 (8)
C(21)	0.2477 (11)	0.3535 (10)	0.6288 (8)
C(22)	0.2204 (12)	0.2572 (10)	0.7437 (9)
C(23)	0.2790 (12)	0.1187 (11)	0.7491 (10)
C(24)	0.2241 (10)	0.0927 (9)	0.6668 (8)
Cl(1)	0.1242 (4)	0.2217 (4)	0.0508 (3)
Cl(2)	−0.1131 (4)	0.1543 (4)	0.0547 (3)
C(25)	0.0332 (11)	0.1016 (11)	0.1137 (9)

Table 3. Positional Parameters for **3**

atom	x	y	z
Sb(1)	0.03043 (2)	0.06823 (1)	0.05497 (2)
Cl(1)	0.7042(1)	0.16138 (6)	0.2657 (1)
Cl(2)	0.9562 (1)	0.16243 (8)	0.3988 (1)
P(1)	0.06911 (7)	0.04775 (4)	−0.17255 (7)
O(1)	0.1017 (2)	0.0884 (1)	−0.0647 (2)
O(2)	−0.1011 (2)	0.0229 (1)	−0.0639 (2)
O(3)	0.0464 (2)	−0.0285 (1)	−0.1639 (2)
C(1)	0.1872 (3)	0.1041 (2)	0.1840 (3)
C(2)	0.2990 (3)	0.0867 (2)	0.1868 (3)
C(3)	0.3995 (3)	0.1090 (2)	0.2723 (4)
C(4)	0.3900 (4)	0.1486 (2)	0.3538 (3)
C(5)	0.2797 (4)	0.1655 (2)	0.3529 (3)
C(6)	0.1780 (3)	0.1434 (2)	0.2671 (3)
C(7)	−0.0741 (3)	0.1586 (2)	0.0273 (3)
C(8)	−0.1979 (3)	0.1540 (2)	−0.0164 (3)
C(9)	−0.2668 (3)	0.2119 (2)	−0.0341 (3)
C(10)	−0.2125 (3)	0.2745 (2)	−0.0087 (3)
C(11)	−0.0908 (3)	0.2800 (2)	0.0316 (3)
C(12)	−0.0212 (3)	0.2221 (2)	0.0499 (3)
C(13)	0.1988 (3)	0.0563 (2)	−0.2086 (3)
C(14)	0.1749 (3)	0.0373 (2)	−0.3291 (3)
C(15)	0.2257 (3)	0.0877 (2)	−0.3883 (3)
C(16)	0.3605 (3)	0.0952 (2)	−0.3510 (3)
C(17)	0.4257 (3)	0.1226 (2)	−0.2345 (3)
C(18)	0.4876 (3)	0.0694 (2)	−0.1488 (3)
C(19)	0.4133 (3)	0.0071 (2)	−0.1487 (3)
C(20)	0.3028 (3)	0.0181 (2)	−0.1223 (3)
C(21)	−0.0626 (3)	0.0875 (2)	−0.2711 (3)
C(22)	−0.1318 (3)	0.0431 (2)	−0.3719 (3)
C(23)	−0.2629 (4)	0.0369 (3)	−0.4003 (4)
C(24)	−0.3419 (4)	0.0925 (3)	−0.4197 (7)
C(25)	−0.3284 (4)	0.1526 (3)	−0.3472 (4)
C(26)	−0.2437 (5)	0.2095 (2)	−0.3365 (5)
C(27)	−0.1404 (4)	0.2003 (2)	−0.3724 (4)
C(28)	−0.0346 (3)	0.1597 (2)	−0.2969 (3)
C(29)	0.8486 (4)	0.1697 (2)	0.2669 (4)

nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions. For **5**, Sb and P atoms were refined anisotropically and the remaining nonhydrogen atoms were refined isotropically; all of the hydrogen atoms except those bonded to the solvent molecule were generated on the basis of geometry considerations. Although the solvent is disordered in **5**, the positions of the carbon and chlorine atoms refined reasonably well, giving satisfactory bond parameters.

Results and Discussion

The dimeric compounds $[Ph_2Sb(O_2PR_2)O]_2$ (R = cyclo-C_6H_{11} (**2**), cycl-C_8H_{15} (**3**)) have been synthesized by two different routes (eq 1). The ^{31}P NMR spectra of **2** and **3** show a single

$$Ph_2SbCl_3 + 3AgO_2CMe \xrightarrow[\text{route A}]{+R_2POOH\ (+H_2O)}$$

$$Ph_2SbCl_3 + 3AgO_2PR_2 \xrightarrow[\text{route B}]{24\ h\ (H_2O)} \longrightarrow [Ph_2Sb(O_2PR_2)O]_2 \quad (1)$$

$$R = \text{cycl-}C_6H_{11} \ (2),$$
$$\text{cycl-}C_8H_{15} \ (3)$$

resonance at 64.3 and 69.6 ppm, respectively, and are consistent with a dimeric structure in solution with a single phosphorus environment. For both of the compounds route A utilizing silver acetate affords the best yields of the pure products. In this route the initially formed acetate $Ph_2Sb(O_2CMe)_3$ is very moisture-sensitive and presumably hydrolyzes to give $[Ph_2Sb(O_2CMe)_2]_2O$ as reported in the literature.[2] Upon addition of the

(8) (a) Calbrese, J. C. *PHASE-Patterson Heavy Atom Solution Extractor.* Ph.D. Thesis, University of Wisconsin−Madison, 1972. (b) Beurskens, P. T. *DIRDIF: Direct Methods for Difference Structures−An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*; Technical Report 1984/1, Crystallography Laboratory, Toernooiveld: Nijmegen, Netherlands.

(9) (a) *TEXSAN, Texray Structure Analysis Package*; Molecular Structure Corp.: The Woodlans, TX, 1987 (revised). (b) Sheldrick, G. M. *SHELX-86: Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986. (c) Sheldrick, G. M. *SHELXL-93: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

phosphinic acid, two of the acetates may be replaced to give a mixed acetate−phosphinate; in fact, in the case of dicyclohexylphosphinic acid, when the reaction time after adding the acid was reduced, we have been able to isolate the mixed acetate−phosphinate, $[Ph_2Sb(O_2CMe)(O_2P(C_6H_{11})_2)]_2O$ (**4**) (^{31}P NMR: 53.1 ppm). Product **4**, although isolatable, is moisture sensitive. If the reaction is allowed to continue for a longer time or if **4** is crystallized in open air, adventitious moisture is sufficient to hydrolyze this intermediate to **2** (eq 2). Such a feature is observed for other antimony carboxylates also.[1,2]

$$[Ph_2Sb(O_2CMe)(O_2P(C_6H_{11})_2)]_2O \xrightarrow[-2CH_3COOH]{H_2O}$$
$$\mathbf{4}$$

$$[Ph_2Sb(O_2P(C_6H_{11})_2O]_2 \quad (2)$$
$$\mathbf{2}$$
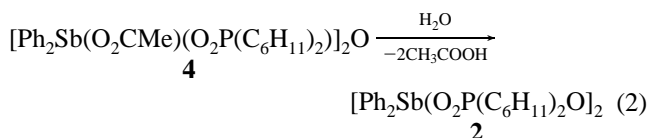
In the second method (route B) for the synthesis of **2**, the chloro compound[1] $[Ph_2SbCl(O_2PC_6H_{11})_2)]_2O$ [^{31}P NMR: 54.6 ppm] which we have reported before is a minor product; indeed if the reaction is not allowed to continue for longer than 2 h, this chloro compound becomes the major product.

Both compounds **2** and **3** are fairly stable in air; however, when **2** is heated with a mixture of acetic acid and water, the tetrameric cage $Ph_8Sb_4O_4(OH)_2(O_2P(C_6H_{11})_2)_2 \cdot CH_3COOH$ (**5** without CH_2Cl_2) is obtained in good yield (eq 3); this compound

$$2[Ph_2Sb(O_2P(C_6H_{11})_2)O]_2 \xrightarrow{CH_3COOH\ +\ 2H_2O}$$
$$Ph_8Sb_4O_4(OH)_2(O_2P(C_6H_{11})_2)_2 \cdot CH_3COOH +$$
$$2(C_6H_{11})_2POOH \quad (3)$$

was initially obtained in an attempt to crystallize the products from the reaction shown in eq 1 (route A). Compound **5** also

Table 4. Positional Parameters for **5**

atom	x	y	z	atom	x	y	z
Sb(1)	0.32519(9)	0.27922(5)	0.73455(7)	C(29)	0.763(2)	0.0795(9)	0.740(1)
Sb(2)	0.33668(8)	0.14653(5)	0.73456(8)	C(30)	0.672(1)	0.0901(8)	0.715(1)
Sb(3)	0.50527(8)	0.15003(5)	0.64789(8)	C(31)	0.494(1)	0.1445(7)	0.534(1)
Sb(4)	0.48313(8)	0.28194(6)	0.63807(7)	C(32)	0.412(1)	0.1481(8)	0.486(1)
Cl(1)	0.636(1)	0.3406(7)	0.9166(9)	C(33)	0.406(2)	0.1397(9)	0.411(1)
Cl(2)	0.599(1)	0.2372(7)	0.884(1)	C(34)	0.482(2)	0.1313(9)	0.384(1)
P(1)	0.3984(4)	0.0460(2)	0.6604(3)	C(35)	0.564(2)	0.1292(9)	0.427(1)
P(2)	0.3599(4)	0.3815(2)	0.6472(3)	C(36)	0.571(1)	0.1353(8)	0.505(1)
O(1)	0.3395(7)	0.0735(4)	0.7039(6)	C(37)	0.472(1)	0.2764(7)	0.5230(10)
O(2)	0.4779(7)	0.0753(4)	0.6462(6)	C(38)	0.393(1)	0.2854(8)	0.477(1)
O(3)	0.3118(8)	0.3541(4)	0.6990(6)	C(39)	0.389(1)	0.2800(9)	0.400(1)
O(4)	0.4243(8)	0.3507(4)	0.6129(6)	C(40)	0.463(2)	0.2730(8)	0.373(1)
O(5)	0.4558(7)	0.2925(4)	0.7386(6)	C(41)	0.543(2)	0.2630(8)	0.419(1)
O(6)	0.3495(8)	0.2590(5)	0.6277(6)	C(42)	0.551(1)	0.2653(7)	0.497(1)
O(7)	0.4804(7)	0.1440(5)	0.7549(7)	C(43)	0.614(1)	0.3128(6)	0.6671(10)
O(8)	0.3709(8)	0.1593(4)	0.6377(7)	C(44)	0.634(1)	0.3540(8)	0.631(1)
O(9)	0.5306(7)	0.2176(5)	0.6629(6)	C(45)	0.722(2)	0.3727(9)	0.649(1)
O(10)	0.3448(7)	0.2130(5)	0.7654(6)	C(46)	0.786(2)	0.3510(9)	0.700(1)
O(11)	0.478(1)	0.4651(9)	0.414(1)	C(47)	0.765(2)	0.3110(9)	0.738(1)
O(12)	0.575(1)	0.4527(6)	0.5203(10)	C(48)	0.677(1)	0.2926(8)	0.719(1)
C(1)	0.181(1)	0.2767(7)	0.691(1)	C(49)	0.441(1)	−0.0070(7)	0.713(1)
C(2)	0.125(1)	0.2928(7)	0.7380(10)	C(50)	0.369(2)	−0.0381(9)	0.732(1)
C(3)	0.032(1)	0.2920(8)	0.714(1)	C(51)	0.403(2)	−0.0789(10)	0.783(2)
C(4)	−0.001(1)	0.2765(8)	0.645(1)	C(52)	0.464(2)	−0.0640(10)	0.848(1)
C(5)	0.053(2)	0.2604(8)	0.599(1)	C(53)	0.539(2)	−0.0310(9)	0.833(1)
C(6)	0.145(1)	0.2596(7)	0.624(1)	C(54)	0.501(2)	0.0104(10)	0.782(1)
C(7)	0.325(1)	0.3034(7)	0.8454(10)	C(55)	0.335(1)	0.0321(7)	0.572(1)
C(8)	0.341(1)	0.3490(9)	0.866(1)	C(56)	0.243(1)	0.0061(8)	0.574(1)
C(9)	0.336(2)	0.363(1)	0.941(2)	C(57)	0.184(2)	0.0028(9)	0.495(1)
C(10)	0.319(2)	0.3309(9)	0.986(1)	C(58)	0.240(2)	−0.0229(10)	0.445(1)
C(11)	0.310(2)	0.284(1)	0.970(1)	C(59)	0.334(2)	0.001(1)	0.446(2)
C(12)	0.309(1)	0.2690(7)	0.895(1)	C(60)	0.386(1)	0.0055(9)	0.522(1)
C(13)	0.338(1)	0.1210(7)	0.841(1)	C(61)	0.423(1)	0.4323(7)	0.692(1)
C(14)	0.387(1)	0.1441(7)	0.902(1)	C(62)	0.363(1)	0.4660(7)	0.726(1)
C(15)	0.389(1)	0.1274(8)	0.972(1)	C(63)	0.417(1)	0.5089(8)	0.762(1)
C(16)	0.342(2)	0.0887(9)	0.981(1)	C(64)	0.498(2)	0.4956(9)	0.816(1)
C(17)	0.289(2)	0.0636(9)	0.923(1)	C(65)	0.554(2)	0.4581(10)	0.787(1)
C(18)	0.290(1)	0.0807(8)	0.851(1)	C(66)	0.505(2)	0.4159(9)	0.747(1)
C(19)	0.195(1)	0.1450(7)	0.692(1)	C(67)	0.275(1)	0.4053(7)	0.572(1)
C(20)	0.162(1)	0.1262(8)	0.622(1)	C(68)	0.205(1)	0.3669(7)	0.546(1)
C(21)	0.071(2)	0.1229(8)	0.595(1)	C(69)	0.135(2)	0.3863(9)	0.481(1)
C(22)	0.011(2)	0.1343(8)	0.642(1)	C(70)	0.178(2)	0.4042(8)	0.425(1)
C(23)	0.045(1)	0.1520(8)	0.710(1)	C(71)	0.249(2)	0.4450(9)	0.448(1)
C(24)	0.137(1)	0.1560(7)	0.736(1)	C(72)	0.319(2)	0.4247(9)	0.513(1)
C(25)	0.644(1)	0.1330(7)	0.6879(10)	C(73)	0.551(2)	0.393(1)	0.421(2)
C(26)	0.707(1)	0.1692(8)	0.683(1)	C(74)	0.541(2)	0.440(1)	0.459(2)
C(27)	0.801(2)	0.1578(9)	0.710(1)	C(75)	0.688(2)	0.282(1)	0.937(1)
C(28)	0.823(2)	0.1140(9)	0.743(1)				

shows a single resonance in the ^{31}P NMR spectrum at 57.7 ppm, showing that the two phosphinates are in an identical chemical environment (see below for structure). Under similar experimental conditions compound **3** does not hydrolyze to any significant extent.

What is perhaps more interesting is the observation that we were able to convert the tetrameric cage **5** back to the dimer **2** by heating the former with an excess of dicyclohexylphosphinic acid (eq 4). The ^{31}P NMR spectrum of the reaction mixture

$$Ph_8Sb_4O_4(OH)_2(O_2P(C_6H_{11})_2)_2 \cdot CH_3COOH +$$

$$3(C_6H_{11})_2POOH \xrightarrow[\text{4 h}]{\text{toluene}} 2[Ph_2Sb(O_2P(C_6H_{11})_2)O]_2 +$$

$$(C_6H_{11})_2POOH + CH_3COOH + 2H_2O \quad (4)$$
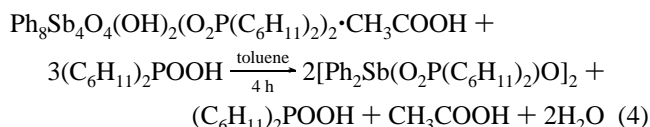
showed compound **2** to be the major product [$\delta = 64.3$ ppm; >85%]; two minor products [$\delta = 53.8$ and 45.9 ppm with total intensity < 10%)] were also observed. Earlier we have demonstrated the interconversion between the two carboxylates [Ph$_2$Sb(O$_2$CMe)$_2$]$_2$O and Ph$_8$Sb$_4$O$_6$(HO$_2$CMe)$_3$.[1] Thus it appears that the Sb−O bonds in these compounds are quite labile; such a feature is reminiscent of the interconversion observed in *n*-butyltin oxocarboxylates/-phosphinates.[10]

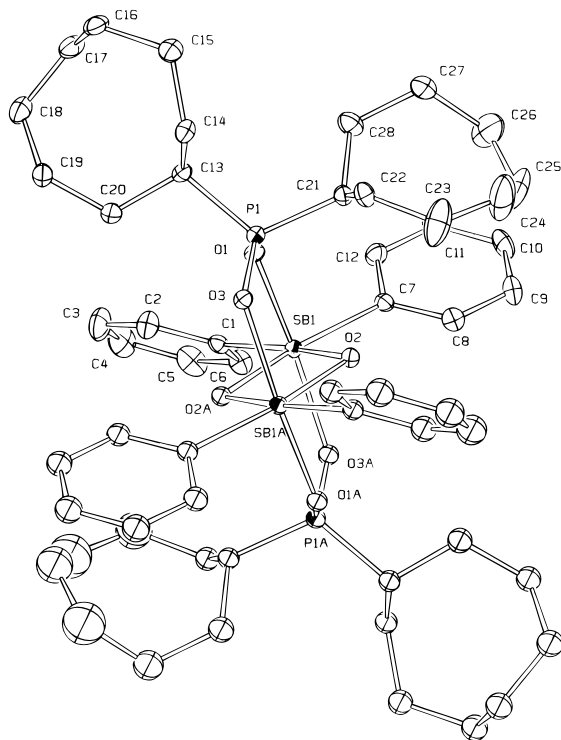(10) Holmes, R. R. *Acc. Chem. Res.* **1989**, 22, 190.
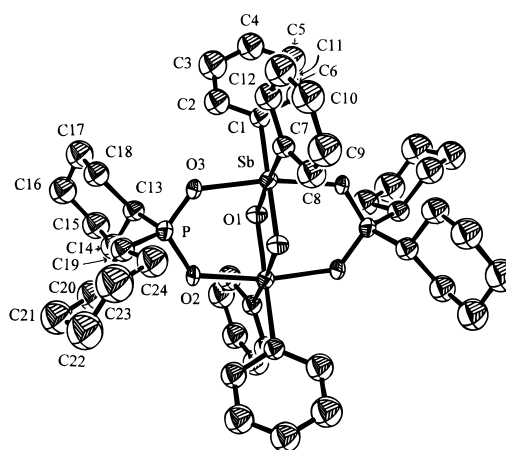
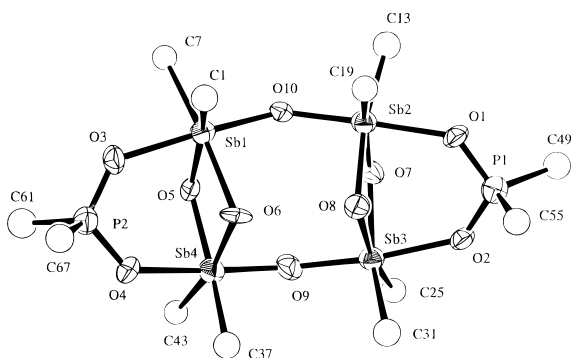**Figure 1.** Molecular structure of **2**. H atoms and the solvent molecule not shown.

Structural Aspects

The molecular structures of compounds **2**, **3**, and **5** are depicted in Figures 1−3.) Selected bond distances and bond angles are provided in Tables 5−7. All three compounds possess four membered Sb−O−Sb−O rings with bridging phosphinates and hexacoordinated antimony. In **5** the two

Figure 2. Molecular structure of **3**. H atoms and the solvent molecule not shown.

Figure 3. Molecular structure of **5** showing the skeleton. C atoms of the phenyl, cyclohexyl, acetic acid, and solvent as well as H atoms are omitted for clarity.

Table 5. Bond Lengths (Å) and Bond Angles (deg) with Esds in Parentheses for **2** (Atoms Related by a Center of Symmetry Given the Suffix A)

|			
Sb−O(1)	1.986(5)	P−O(2)	1.530(5)
Sb−O(1A)	1.982(5)	P−O(3)	1.538(5)
Sb−O(2A)	2.115(5)	P−C(13)	1.794(8)
Sb−O(3)	2.112(5)	P−C(19)	1.805(8)
Sb−C(1)	2.147(8)	Sb−Sb(A)	3.019(4)
O(1A)−Sb−O(1)	80.9(2)	O(2A)−Sb−C(1)	92.0(3)
O(1A)−Sb−O(3)	86.6(2)	C(7)−Sb−C(1)	99.4(3)
O(1)−Sb−O(3)	85.6(2)	O(3)−Sb−C(1)	95.4(3)
O(1A)−Sb−O(2A)	84.6(2)	O(2)−P−O(3)	116.7(3)
O(1)−Sb−O(2A)	86.3(2)	O(2)−P−C(13)	108.6(3)
O(1A)−Sb−C(7)	91.7(3)	O(2)−P−C(19)	106.3(3)
O(3)−Sb−C(7)	93.9(3)	O(3)−P−C(13)	106.2(3)
O(3)−Sb−O(2A)	168.9(2)	O(3)−P−C(19)	107.0(3)
O(1)−Sb−C(7)	172.7(2)	C(13)−P−C(19)	112.2(4)
O(2A)−Sb−C(7)	93.1(3)	Sb(A)−O(1)−Sb	99.1(2)
O(1)−Sb−C(1)	87.9(3)	P−O(2)−Sb(A)	126.8(3)
O(1A)−Sb−C(1)	168.5(2)	P−O(3)−Sb	125.6(3)

Sb$_2$O$_2$ rings are connected through oxo bridges between the antimony atoms to form an Sb$_4$O$_6$ cage, and the structure can be described as a crown.[3] The bridging phosphinates in **2**, **3**, and **5** are *cis* to the phenyl groups on antimony. Thus the three

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) with Esds in Parentheses for **3** (Atoms Related by a Center of Symmetry Given the Suffix A)

Sb(1)−O(1)	2.100(2)	P(1)−O(1)	1.546(2)
Sb(1)−O(2)	1.975(2)	P(1)−O(3)	1.542(2)
Sb(1)−O(2A)	1.977(2)	P(1)−C(13)	1.812(3)
Sb(1)−O(3A)	2.132(2)	P(1)−C(21)	1.811(3)
Sb(1)−C(1)	2.134(3)	Sb(1)···Sb(1A)	3.0142(5)
Sb(1)−C(7)	2.137(3)		
O(1)−Sb(1)−O(2)	85.97(8)	O(3A)−Sb(1)−C(1)	94.1(1)
O(1)−Sb(1)−O(2A)	85.74(8)	O(3A)−Sb(1)−C(7)	92.3(1)
O(1)−Sb(1)−O(3A)	168.99(8)	C(1)−Sb(1)−C(7)	98.7(1)
O(1)−Sb(1)−C(1)	92.2(1)	O(1)−P(1)−O(3)	115.5(1)
O(1)−Sb(1)−C(7)	95.7(1)	O(1)−O(1)−C(13)	104.2(1)
O(2)−Sb(1)−O(2A)	80.6(1)	O(1)−P(1)−C(21)	106.4(1)
O(2)−Sb(1)−O(3A)	86.51(8)	O(3)−P(1)−C(13)	107.9(1)
O(2)−Sb(1)−C(1)	171.6(1)	O(3)−P(1)−C(21)	110.0(1)
O(2)−Sb(1)−C(7)	89.7(1)	C(13)−P(1)−C(21)	112.9(2)
O(2A)−Sb(1)−O(3A)	85.10(8)	Sb(1)−O(1)−P(1)	123.7(1)
O(2A)−Sb(1)−C(1)	91.1(1)	Sb(1A)−O(3)−P(1)	123.0(1)
O(2A)−Sb(1)−C(7)	170.1(1)	Sb(1)−O(2)−Sb(1A)	99.4(1)

compounds represent new structural types for antimony phosphinates.

The Sb−O−Sb−O rings **2** and **3** are nearly planar; however, the angles at the oxygen atoms are wider [99.1(2)° for **2** and 99.4(1)° for **3**] at the expense of those at antimony [80.9(2)° for **2** and 80.6(1)° for **3**] in both of the dinuclear compounds. It is interesting to note that diminution of the angle at antimony is found even at pentacoordinated antimony in [Ph$_3$SbO]$_2$ (**III**)
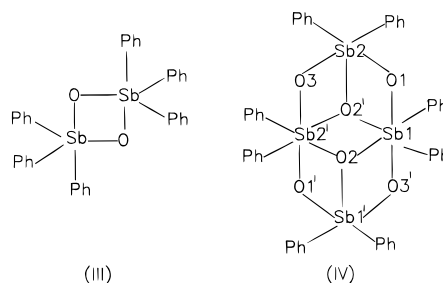
(77.4°)[11] and the fused ring system in Ph$_8$Sb$_4$O$_6$ (**IV**) (76°),[12] both of which contain the Sb$_2$O$_2$ ring system. The Sb−O distances within the four membered ring in **2** [mean = 1.984 Å] are shorter than the Sb−O distances to the bridging phosphinates but are longer than the Sb−O(oxo) distances in [Ph$_2$SbCl(O$_2$P(C$_6$H$_{11}$)$_2$)]$_2$O (**I**) [1.936(4) and 1.938(4) Å; mean = 1.937 Å] and [Cl$_3$Sb(O$_2$PMe$_2$)]$_2$O [1.942(2) Å].[13] The transoidal orientation of phosphinates in **2** and **3** as compared to cisoidal in **I** is most likely due to a restriction imposed by the formation of the Sb$_2$O$_2$ ring.

An interesting correlation exists between the compound Ph$_8$-Sb$_4$O$_6$ (**IV**) and our compounds **2** and **3**. Removal of the two bonds Sb(2)−O(2) and Sb(1)−O(2) from **IV** will lead to the same skeleton as that observed for **2** or **3**, with the antimony atoms Sb(2) and Sb(1)′ (in **IV**) being replaced by the phosphorus atoms (in **2** or **3**). In fact in the original paper[12] the authors suggest such a canonical structure for **IV**.

In compound **5** charge balance would require the formula for the unsolvated molecule to be written as Ph$_8$Sb$_4$O$_4$(OH)$_2$-(O$_2$P(C$_6$H$_{11}$)$_2$)$_2$. In the actual structure, an acetic acid molecule, unconnected to the antimony cage even by H bonding, is also present. On the basis of the bond length data (Table 7) we propose that the oxygen atoms O(6) and O(7) of the cage are

(11) Ferguson, G.; Glidewell, C.; Kaitner, B.; Lloyd, D.; Metcalfe, S. *Acta Crystallogr.* **1987**, *C43*, 824.

(12) Bordner, J.; Doak, G. O.; Everett, T. S. *J. Am. Chem. Soc.* **1986**, *108*, 4206.

(13) Blösl, S.; Schwarz, W.; Schmidt, A. *Z. Naturforsch.* **1984**, *38B*, 143.

**Table 7.** Selected Interatomic Distances (Å) and Bond Angles (deg) with Esds in Parentheses for **5**

Sb(1)−O(5)	2.00(1)	Sb(3)−C(25)	2.14(2)
Sb(1)···O(6)	2.17(1)	Sb(3)−C(31)	2.11(2)
Sb(1)−O(3)	2.19(1)	Sb(4)−O(5)	2.02(1)
Sb(1)−O(10)	1.94(1)	Sb(4)−O(6)	2.09(1)
Sb(1)−C(1)	2.17(2)	Sb(4)−O(4)	2.13(1)
Sb(1)−C(7)	2.18(2)	Sb(4)−O(9)	1.95(1)
Sb(2)−O(8)	2.01(1)	Sb(4)−C(37)	2.13(2)
Sb(2)−O(7)	2.13(1)	Sb(4)−C(43)	2.13(2)
Sb(2)−O(1)	2.12(1)	O(1)−P(1)	1.52(1)
Sb(2)−O(10)	1.93(1)	P(1)−O(2)	1.52(1)
Sb(2)−C(13)	2.10(2)	O(3)−P(2)	1.52(1)
Sb(2)−C(19)	2.14(2)	P(2)−O(4)	1.53(1)
Sb(3)−O(8)	2.02(1)	Sb(1)−Sb(4)	3.257(2)
Sb(3)−O(7)	2.11(1)	Sb(2)−Sb(3)	3.270(2)
Sb(3)−O(2)	2.12(1)	O(11)···O(12)[a]	2.79(3)
Sb(3)−O(9)	1.93(1)	O(6)···O(8)	2.80(2)
O(3)−Sb(1)−O(5)	82.3(5)	O(7)−Sb(3)−O(9)	90.3(5)
O(3)−Sb(1)−O(6)	89.5(5)	O(7)−Sb(3)−C(25)	89.6(6)
O(3)−Sb(1)−O(10)	176.5(4)	O(7)−Sb(3)−C(31)	162.9(6)
O(3)−Sb(1)−C(1)	83.7(6)	O(8)−Sb(3)−O(9)	93.2(5)
O(3)−Sb(1)−C(7)	88.6(6)	O(8)−Sb(3)−C(25)	164.0(6)
O(5)−Sb(1)−O(6)	75.0(4)	O(8)−Sb(3)−C(31)	91.6(6)
O(5)−Sb(1)−O(10)	94.2(5)	O(9)−Sb(3)−C(25)	90.7(6)
O(5)−Sb(1)−C(1)	158.9(6)	O(9)−Sb(3)−C(31)	101.2(7)
O(5)−Sb(1)−C(7)	95.0(6)	C(25)−Sb(3)−C(31)	102.8(8)
O(6)−Sb(1)−O(10)	89.0(5)	O(4)−Sb(4)−O(5)	85.6(5)
O(6)−Sb(1)−C(1)	89.1(6)	O(4)−Sb(4)−O(6)	84.3(5)
O(6)−Sb(1)−C(7)	170.0(6)	O(4)−Sb(4)−O(9)	176.6(5)
O(10)−Sb(1)−C(1)	99.4(6)	O(4)−Sb(4)−C(37)	83.9(6)
O(10)−Sb(1)−C(7)	92.3(6)	O(4)−Sb(4)−C(43)	91.2(6)
C(1)−Sb(1)−C(7)	100.5(7)	O(5)−Sb(4)−O(6)	76.4(5)
O(1)−Sb(2)−O(7)	86.8(5)	O(5)−Sb(4)−O(9)	92.6(5)
O(1)−Sb(2)−O(8)	84.6(5)	O(5)−Sb(4)−C(37)	163.3(6)
O(1)−Sb(2)−O(10)	175.3(4)	O(5)−Sb(4)−C(43)	92.9(6)
O(1)−Sb(2)−C(13)	86.2(6)	O(6)−Sb(4)−O(9)	92.6(5)
O(1)−Sb(2)−C(19)	87.1(6)	O(6)−Sb(4)−C(37)	89.7(6)
O(7)−Sb(2)−O(8)	74.7(5)	O(6)−Sb(4)−C(43)	168.7(6)
O(7)−Sb(2)−O(10)	88.5(5)	O(9)−Sb(4)−C(37)	97.3(6)
O(7)−Sb(2)−C(13)	89.7(6)	O(9)−Sb(4)−C(43)	91.7(6)
O(7)−Sb(2)−C(19)	168.1(6)	C(37)−Sb(4)−C(43)	100.2(7)
O(8)−Sb(2)−O(10)	94.9(5)	O(1)−P(1)−O(2)	112.8(7)
O(8)−Sb(2)−C(13)	162.2(6)	O(3)−P(2)−O(4)	113.9(7)
O(8)−Sb(2)−C(19)	94.5(6)	Sb(2)−O(1)−P(1)	132.2(7)
O(10)−Sb(2)−C(13)	93.1(6)	Sb(3)−O(2)−P(1)	133.2(7)
O(10)−Sb(2)−C(19)	97.6(6)	Sb(1)−O(3)−P(2)	130.1(7)
C(13)−Sb(2)−C(19)	100.1(7)	Sb(4)−O(4)−P(2)	133.3(8)
O(2)−Sb(3)−O(7)	82.3(5)	Sb(1)−O(5)−Sb(4)	108.4(5)
O(2)−Sb(3)−O(8)	86.3(5)	Sb(1)−O(6)−Sb(4)	99.6(5)
O(2)−Sb(3)−O(9)	172.5(5)	Sb(2)−O(7)−Sb(3)	100.9(5)
O(2)−Sb(3)−C(25)	87.8(6)	Sb(2)−O(8)−Sb(3)	108.7(5)
O(2)−Sb(3)−C(31)	86.3(6)	Sb(3)−O(9)−Sb(4)	143.8(6)
O(7)−Sb(3)−O(8)	74.9(5)	Sb(1)−O(10)−Sb(2)	145.6(6)

[a] Intermolecular distance.

protonated; it can be readily seen that Sb−O distances to these oxygen atoms are longer than the other nonphosphinate Sb−O distances [to O(5), O(8), O(9), and O(10)].

Compared to **2**, the Sb_2O_2 rings in **5** are slightly nonplanar with a maximum deviation of atoms being ≤0.1 Å from the mean plane. What is more interesting in **5**, however, is the dihedral angle between the two Sb_2O_2 rings [Sb(4)−O(5)−Sb-(1)−O(6) and Sb(2)−O(7)−Sb(3)−O(8)] which is 30°. This makes the atoms O(6) and O(8) come closer (2.80 Å); simultaneously, O(5) and O(7) move farther apart (4.18 Å). The O(6)−O(8) distance is appropriate for a proton to sit between. In the X-ray structure of the acetate analogue $Ph_8Sb_4O_6(HO_2-CMe)_3 \cdot CH_2Cl_2$ (**IV**) of **5**, which has been described briefly in a communication,[2] a proton resides between the atoms corresponding to O(6) and O(8) [O···O distance in **V**: 2.63 Å]. However, in the acetate cage **V** an acetic acid molecule bridges the oxygens corresponding to O(5) and O(7) by H bonding; such a feature is absent in compound **5**. The acetate group in **5** exists as acetic acid and is neutral; this conclusion is based on the intermolecular H bond between the two oxygens [O(11)···O(12′) = 2.79(3) Å] of the acetic acid.
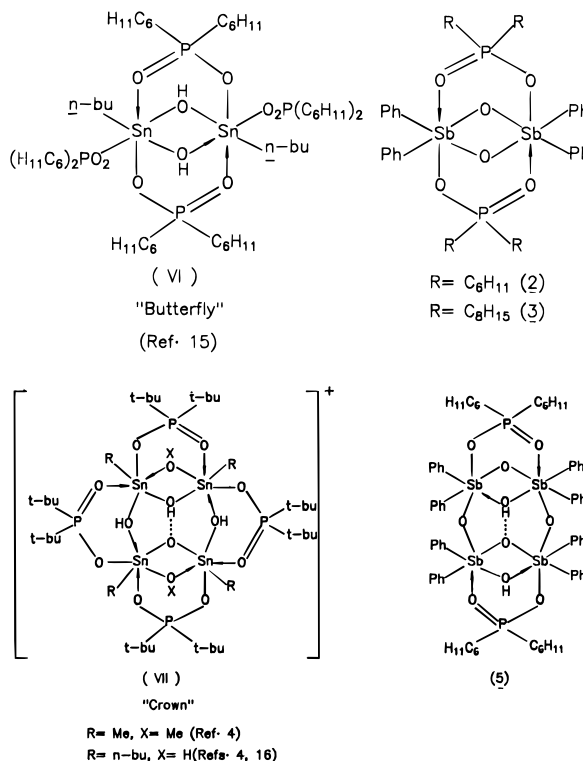
In connection with the Sb_4O_6 skeleton that we observe in **5**, it is instructive to note that a second alternative structure (**A**)

(A)
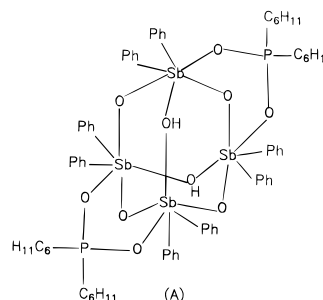
with an "adamantane" type of skeleton is possible. From the molecular models at least, there does not appear to be any severe strain in such a structure. Since such a cage for hexacoordinated manganese has already been found,[14] we believe that the crown structure observed for **5** is a result of the reaction pathway rather than any special preference for the observed structure.

Analogy to Tin Structures

In hexacoordinated systems, five covalent and one coordinate bond would make antimony(V) electronically equivalent to tin-(IV) with four covalent and two coordinate bonds. Hence structural analogies can be expected between Sn(IV) and Sb-(V) derivatives. Thus compounds **2**, **3**, and **5** are structurally equivalent to the "butterfly" (**VI**)[15] and crown (**VII**) structures reported for tin.

(VI)
"Butterfly"
(Ref· 15)

R= C_6H_{11} (**2**)
R= C_8H_{15} (**3**)

(VII)
"Crown"
R= Me, X= Me (Ref· 4)
R= n-bu, X= H(Refs· 4, 16)

(**5**)

To summarize, two new structural forms, one with a dinuclear Sb_2O_2 skeleton and the other with a tetranuclear Sb_4O_6 cage for oxoantimony phosphinates, have been uncovered. It should be possible to synthesize other structural forms (such as the adamantane **A**) with oxo bridges. Indeed in the reactions using

(14) Hagen, K. S.; Westmoreland, T. D.; Scott, M. J.; Armstrong, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 1907.
(15) Holmes, R. R.; Kumara Swamy, K. C.; Schmid, C. G.; Day, R. O. *J. Am. Chem. Soc.* **1988**, *110*, 7060.
(16) Kumara Swamy, K. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 4184.

dicyclohexylphosphinic acid we have identified a new compound [δ(^{31}P): 45.9 ppm] in addition to the structurally characterized derivatives [Ph$_2$SbCl(O$_2$P(C$_6$H$_{11}$)$_2$)]$_2$O,[1] [Ph$_2$Sb-(O$_2$P(C$_6$H$_{11}$)$_2$)O]$_2$·CH$_2$Cl$_2$ (**2**), and Ph$_8$Sb$_4$O$_4$(OH)$_2$(O$_2$P(C$_6$H$_{11}$)$_2$)· CH$_3$COOH·CH$_2$Cl$_2$ (**5**). Efforts are underway to isolate and characterize this new compound.

Supporting Information Available: Listings of anisotropic thermal parameters (Tables S1−S3) and bond lengths and angles (Tables S4− S6) and an ORTEP diagram of **5** showing all the atoms in the skeleton (14 pages). Ordering information is given on any current masthead page.

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