and suggests bonding of an analogous nature.[21,22] Assuming this to be true, the metal ion should be in a tripositive oxidation state and should supply electrons into conduction bands. In this phase, each neodymium ion could presumably donate one-half electron to the conduction band, assuming all carbon units exist as C^{4-} ions and the stoichiometry is Nd_4O_3C. The silver-gray color of the phase is also indicative of conduction band occupation, but further conductivity and magnetic studies are needed before definite statements can be made about the bonding.

Acknowledgment. The partial support of the U. S. Atomic Energy Commission (COO-716-030) is gratefully acknowledged. The help of D. Cromer, Los Alamos Scientific Laboratory (program, Antifact), Dow Chemical Co., Midland, Mich. (X-ray diffractometer time), and J. A. Steward (undergraduate assistant) are appreciated.

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Crystal and Molecular Structures of Methoxytetraphenylantimony and Dimethoxytriphenylantimony

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Abstract: The structures of methoxytetraphenylantimony, $(C_6H_5)_4SbOCH_3$, and dimethoxytriphenylantimony, $(C_6H_5)_3Sb(OCH_3)_2$, have been determined from three-dimensional single crystal X-ray diffraction counter data. Both compounds are monomeric and contain pentacoordinated antimony atoms. Methoxytetraphenylantimony crystallizes with eight molecules in space group Pbca of the orthorhombic system with cell dimensions of $a = 14.81$ (2), $b = 16.95$ (3), $c = 16.74$ (2) Å; $V = 4202$ Å^3. The conformation of the organic ligands around the antimony atom is that of a trigonal bipyramid with the methoxyl group occupying one of the apical positions. The Sb–O bond distance is 2.061 (7) Å. The apical Sb–C bond distance of 2.199 (14) Å is significantly longer than the equatorial Sb–C distances of 2.131 (11), 2.128 (13), and 2.097 (15) Å. The Sb atom is displaced 0.10 Å out of the equatorial plane toward the apical phenyl group. Dimethoxytriphenylantimony crystallizes with four molecules in space group $P2_1/c$ of the monoclinic system with cell dimensions of $a = 11.51$ (2), $b = 9.40$ (2), $c = 17.30$ (3) Å; $\beta = 101.75$ (1)°; $V = 1832$ Å^3. The trigonal bipyramidal conformation around the antimony atom has a carbon atom from each of the three benzene rings in the equatorial plane with Sb–C distances of 2.119 (10), 2.121 (11), and 2.119 (12) Å. The methoxyl groups occupy both apical positions with Sb–O bond distances of 2.039 (8) and 2.027 (8) Å. The conventional crystallographic R factors are respectively 2.8 and 3.4%. The nmr spectrum of methoxytetra-*p*-tolylantimony has been taken and a single sharp peak was observed for the *p*-methyl protons. This result suggests that this compound exists in solution either as a rapidly established equilibrium mixture of trigonal-bipyramidal and square-pyramidal configurations or as the latter configuration only.

Methoxytetraphenylantimony and dimethoxytriphenylantimony have been obtained by Briles and McEwen[2] by reaction of tetraphenylstibonium bromide with sodium methoxide in methanol solution. The preparation of the latter compound by this method is of particular interest in that it represents a clear case of a nucleophilic substitution reaction at antimony

$$(C_6H_5)_4Sb^+,Br^- + NaOCH_3 \longrightarrow NaBr +$$

$$(C_6H_5)_4SbOCH_3 \xrightarrow{CH_3OH} (C_6H_5)_3Sb(OCH_3)_2 + C_6H_6$$

Although the subject of pentacoordinate species has, in recent years, received considerable attention,[3] relatively few structures[4-10] of organic antimony(V) compounds containing alkyl or aryl groups have been clearly established. All but one of the known pentacoordinated group V elements adopt a trigonal bipyramidal geometry. The exception is pentaphenylantimony, $Sb(C_6H_5)_5$, which, unlike the phosphorus and arsenic homologs,[11] was found by Wheatley[12] to have an approximately square-pyramidal structure. The difference in energy between the trigonal bipyramid and the square pyramid for most compounds is probably small, and as such there may be specific ligand stabil-

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ization of the latter state. It seemed of particular interest, therefore, to determine the molecular and crystal structures of these compounds as a first step in the study of the stereochemistry of substitution reactions at antimony.

Experimental Section

Preparation. (a) **Methoxytetraphenylantimony (I).** This compound was obtained by the reaction of tetraphenylstibonium bromide with sodium methoxide.[2b] Well-developed, colorless, moisture-sensitive crystals (mp 132°) were obtained by crystallization from anhydrous petroleum ether (bp 60–80°).

(b) **Dimethoxytriphenylantimony (II).** This compound[2] was obtained by the reaction of dibromotriphenylantimony with sodium methoxide.

$$(C_6H_5)_3SbBr_2 + 2NaOCH_3 \longrightarrow (C_6H_5)_3Sb(OCH_3)_2 + NaBr$$

Sublimation of the reaction mixture yielded large, colorless, moisture-sensitive crystals (mp 100–102°).

(c) **Methoxytetra-*p*-tolylantimony (III).** This compound was prepared by the method of Briles.[2b] To a solution of 15 g (0.038 mole) of tri-*p*-tolylstibine (mp 124°, obtained from the reaction of *p*-tolylmagnesium bromide with antimony trichloride) in 50 ml of chloroform, a solution of 6.2 g (0.038 mole) of Br_2 in 20 ml of chloroform was added slowly with stirring. Some precipitate appeared after about half of the bromine solution had been added. After having been stirred for 3 hr, the reaction mixture was concentrated to 20 ml and cooled in a refrigerator overnight. The precipitate which had formed was collected by filtration and crystallized from chloroform and benzene solutions. A total of 16.8 g of tri-*p*-tolylantimony dibromide (mp 233°) was obtained (yield 80%); the nmr spectrum showed a singlet at δ 2.43 ppm (*p*-CH_3, 9 H) and doublets at δ 7.35 and 8.07 ppm (*o*- and *m*-H, respectively, J_{o-m} = 8 cps, 6 H for each doublet). *p*-Tolylmagnesium bromide was prepared from 10 g of *p*-bromotoluene, 0.98 g of Mg, and 80 ml of ether in a flask provided with a stirrer. Tri-*p*-tolylantimony dibromide (15 g, 0.027 mole) dissolved in 80 ml of benzene was added slowly and with stirring to the *p*-tolylmagnesium bromide solution. After the solution had been refluxed for 3 hr, 10 g of ice and 6 ml of 48% hydrobromic acid were added slowly. The ether–benzene layer was separated from the aqueous layer. The ether–benzene solution was evaporated on a steam bath. A gummy residue remained. The residue was washed five times with 50 ml of hot water. The aqueous wash solutions were filtered and concentrated to 150 ml. The solution was cooled in a refrigerator overnight; 6.9 g (45%) of crystalline tetra-*p*-tolylstibonium bromide (mp 223–225°) was obtained. The nmr spectrum ($CDCl_3$) showed a singlet at δ 2.42 ppm (12 H), two doublets at δ 7.35 and 9.07 ppm (*o*- and *m*-H, respectively, J_{o-m} = 8 cps, 8 H for each doublet). *Anal.* Calcd for $C_{28}H_{28}SbBr$: C, 59.39; H, 4.98; Sb, 21.50; Br, 14.12. Found: C, 59.76; H, 5.07; Sb, 21.05; Br, 14.53.

About 0.069 g (0.003 g-atom) of clean sodium was dissolved in 15 ml of anhydrous methanol, and the solution was cooled to room temperature. To this solution was added 1.7 g (0.003 mole) of tetra-*p*-tolylstibonium bromide, and the mixture was refluxed under nitrogen until the solid dissolved. The mixture was allowed to cool to room temperature, and the solvent was evaporated *in vacuo*. The white solid which remained was shaken with two 50-ml portions of anhydrous petroleum ether (B) at room temperature in a dry nitrogen bag. The petroleum ether solutions were combined and the solvent evaporated under vacuum. A white crystalline hygroscopic solid which weighed 0.8 g (yield 55%) was obtained; mp 64–65°. The nmr spectrum showed singlets at δ 2.35 (*p*-CH_3, 12 H) and 2.80 ppm (CH_3O, 3 H) and two doublets at δ 7.10 and 7.49 ppm (*o*- and *m*-H, respectively, 16 H in all, J_{o-m} = 8 cps). The spectrum at −60° ($CDCl_3$–CCl_4 mixture as solvent) did not show any difference from the spectrum at room temperature. *Anal.* Calcd for $C_{29}H_{31}OSb$: C, 67.33; H, 6.04; Sb, 23.54. Found: C, 67.13; H, 6.00; Sb, 23.51.

All nmr spectra were taken on a Varian A-60 spectrometer, in carbon tetrachloride with TMS as internal standard, unless otherwise noted.

Crystallographic Data. The crystallographic data are presented in Table I. There are no symmetry conditions imposed on the molecules of either compound by its space group. Nb-filtered Mo Kα radiation intensity measurements were made on a G.E. XRD5 spectrogoniometer equipped with a single-crystal orienter. A scintillation counter, pulse-height discriminator, and the moving-crystal, moving-counter technique were used.

Table I. Crystallographic Constants of Methoxytetraphenylantimony (I) and Dimethoxytriphenylantimony (II)

	I	II
Molecular weight	461.22	415.15
a, Å	14.81 (2)	11.51 (2)
b, Å	16.95 (3)	9.40 (2)
c, Å	16.74 (2)	7.30 (3)
β, deg	...	101.75 (1)
V, Å^3	4202	1832
Z	8	4
ρ_{obsd}, g/cm^3 [a]	1.44	1.50
ρ_{calcd}, g/cm^3 [a]	1.467	1.505
μ, cm^{-1}	13.51	15.34
Space group	P_{bca}	$P2_{1/c}$
Absent spectra	$hk0$: $h \neq 2n$ $h0l$: $l \neq 2n$ $0kl$: $k \neq 2n$	$h0l$: $l \neq 2n$ $0k0$: $k \neq 2n$

[a] Measured by flotation in solutions of (I) trichloroethylene and *n*-dodecane; (II) 1,2-dibromobutane and *n*-dodecane.

Both compounds were found to deteriorate slowly during X-ray irradiation. For I, two crystals of approximate dimensions 0.35 × 0.3 × 0.3 mm were used to collect 860 observed independent reflections ($0 < 2\theta \leq 40°$). The crystals were sealed in glass capillaries; the first under atmospheric pressure, the second under vacuum. To monitor the decomposition the 215 reflection was measured about every 40 reflections. A linear correction factor was assumed between the monitored points. For both crystals, data collection was terminated when 40% of the initial intensity of the 215 reflection had been lost.

For II a cleaved crystal, of approximate dimensions 0.35 × 0.35 × 0.3 mm and sealed in a glass capillary under dry argon, was used to collect 822 observed independent reflections ($0 < 2\theta \leq 36°$). The 008 reflection served to monitor the decomposition. At the completion of data collection, 50% of the initial intensity had been lost. Structure amplitudes were derived from the intensities by correcting for background, Lorentz, and polarization factors. No absorption corrections were applied.

Solution and Refinement. In each compound, the position of the Sb atom was readily derived from the three-dimensional Patterson function. The light atoms (excluding hydrogen) were easily found in a difference Fourier phased by the antimony contribution. The structural parameters were refined by the full-matrix least-squares method minimizing the quantity $\Sigma w(|F_o|^2 - |F_c|^2)^2$ with weights *w* assigned as follows: $w = ((0.05\,F^2)^2 + \sigma^2)^{-1/2}$, where σ is the estimated variance of F^2 based on the Poisson counting statistics.

The neutral light atom scattering factors, as tabulated in the "International Tables for X-Ray Crystallography,"[13] were used together with the Dirac–Slater scattering factor for Sb.[14] The anomalous dispersion terms for Sb, as determined by Cromer,[15] were also included in the structure factor calculations.[16] The least-

Table II. Crystallographic *R* Values[a]

Refinement	I			II		
	$R_{(F^2)}$	$R_{(F)}$	$R'_{(F^2)}$	$R_{(F^2)}$	$R_{(F)}$	$R'_{(F^2)}$
A	0.094		0.203	0.102		0.162
B	0.070		0.132	0.068		0.106
C	0.052	0.028	0.090	0.058	0.034	0.076
Est std dev of an obsvn of unit wt	1.73			1.63		

[a] $R_{(F^2)} = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$. $R_{(F)} = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R'_{(F^2)} = \sqrt{\Sigma w(F_o^2 - F_c^2)^2}/\sqrt{\Sigma w(F_o^2)^2}$.

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Table III. Final Parameter Values for $(C_6H_5)_4SbOCH_3$

Atom	x	y	z	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	0.12070 (6)[b]	0.20264 (5)	0.04221 (4)	34.6 (8)	42.1 (9)	34.2 (6)	0.5 (5)	−0.4 (5)	17.2 (4)
O	0.1933 (5)	0.1417 (4)	0.1274 (4)	26 (5)	50 (5)	27 (5)	11 (4)	0 (4)	11 (5)
C1	0.1734 (8)	0.1502 (8)	0.2083 (7)	86 (11)	91 (11)	25 (8)	29 (9)	22 (9)	3 (8)
C2	0.2184 (10)	0.1575 (8)	−0.0397 (8)	36 (11)	39 (9)	25 (10)	−2 (9)	4 (8)	-3 (8)
C3	0.2943 (12)	0.1179 (8)	−0.0148 (8)	29 (10)	48 (10)	50 (10)	17 (9)	8 (10)	−5 (8)
C4	0.3572 (9)	0.0891 (8)	−0.0671 (11)	25 (11)	65 (12)	83 (13)	27 (9)	−7 (11)	−1 (10)
C5	0.3446 (11)	0.1047 (8)	−0.1500 (10)	55 (12)	65 (11)	63 (13)	−8 (9)	14 (10)	−9 (10)
C6	0.2713 (12)	0.1458 (9)	−0.1770 (7)	47 (11)	70 (12)	26 (9)	−5 (9)	2 (9)	−6 (9)
C7	0.2095 (10)	0.1730 (7)	−0.1207 (10)	63 (11)	48 (10)	42 (9)	−22 (8)	4 (10)	−7 (9)
C8	0.0056 (7)	0.1373 (6)	0.0805 (6)	27 (12)	36 (14)	37 (8)	6 (10)	−1 (8)	−12 (8)
C9	0.0098 (8)	0.0567 (7)	0.0964 (7)	52 (13)	36 (14)	82 (12)	−7 (12)	21 (9)	20 (9)
C10	−0.0683 (11)	0.0166 (7)	0.1166 (8)	113 (16)	29 (11)	73 (12)	−33 (16)	28 (13)	6 (9)
C11	−0.1495 (8)	0.0545 (9)	0.1239 (8)	35 (14)	83 (20)	71 (12)	−7 (12)	13 (9)	−11 (13)
C12	−0.1536 (8)	0.1350 (8)	0.1097 (7)	70 (18)	60 (15)	47 (10)	5 (12)	−6 (9)	4 (10)
C13	−0.0769 (9)	0.1745 (7)	0.0876 (7)	44 (11)	36 (11)	41 (9)	−17 (12)	9 (9)	−1 (8)
C14	0.0415 (10)	0.2639 (9)	−0.0503 (8)	49 (11)	34 (12)	50 (10)	−7 (10)	−4 (9)	−6 (9)
C15	−0.0218 (11)	0.2244 (8)	−0.0968 (10)	38 (10)	53 (11)	45 (10)	−1 (9)	−4 (9)	−10 (10)
C16	−0.0657 (10)	0.2594 (14)	−0.1586 (10)	49 (11)	101 (17)	44 (11)	26 (13)	−15 (10)	11 (11)
C17	−0.0511 (12)	0.3375 (15)	−0.1764 (8)	52 (14)	114 (17)	36 (10)	21 (13)	−11 (10)	7 (12)
C18	0.0117 (12)	0.3801 (9)	−0.1317 (10)	86 (12)	63 (12)	55 (11)	13 (11)	−26 (11)	32 (11)
C19	0.0574 (9)	0.3442 (10)	−0.0695 (8)	56 (10)	52 (12)	38 (10)	4 (10)	−12 (9)	5 (9)
C20	0.1544 (12)	0.3099 (8)	0.0988 (8)	23 (10)	40 (10)	35 (9)	4 (10)	13 (7)	2 (9)
C21	0.0951 (10)	0.3489 (12)	0.1457 (11)	38 (13)	53 (13)	63 (11)	−10 (10)	−26 (10)	−9 (9)
C22	0.1134 (15)	0.4247 (15)	0.1747 (9)	83 (16)	74 (18)	76 (11)	26 (13)	−40 (13)	−23 (11)
C23	0.1937 (20)	0.4611 (9)	0.1552 (12)	128 (19)	38 (13)	78 (15)	−12 (15)	−37 (15)	−15 (11)
C24	0.2504 (13)	0.4237 (15)	0.1103 (11)	114 (17)	79 (18)	80 (14)	−38 (14)	32 (13)	−8 (12)
C25	0.2339 (14)	0.3456 (13)	0.0814 (8)	69 (14)	83 (16)	44 (9)	−21 (12)	13 (10)	−4 (11)

[a] The general form for the anisotropic temperature factor is $\exp\{-2\pi^2\Sigma_{i,j}h_ih_ja_i{}^*a_j{}^*U_{ij}\}$. Temperature factors and standard deviation are multiplied by 10^3. [b] The estimated standard deviation in the least significant figure is given in parentheses here and in subsequent tables

Table IV. Final Parameter Values for $(C_6H_5)_3Sb(OCH_3)_2$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	−0.24451 (6)	0.21039 (9)	0.18937 (4)	35.9 (6)	40.0 (7)	34.3 (6)	−2.1 (4)	0.1 (4)	2.6 (4)
O1	−0.0660 (6)	0.2455 (7)	0.2114 (4)	36 (5)	47 (6)	50 (5)	−6 (4)	−8 (4)	15 (4)
O2	−0.4192 (6)	0.1599 (7)	0.1708 (4)	33 (5)	48 (5)	51 (5)	3 (4)	10 (4)	4 (4)
C1	−0.0076 (10)	0.3108 (12)	0.1552 (6)	54 (8)	83 (11)	47 (8)	−28 (7)	24 (7)	20 (7)
C2	−0.4913 (10)	0.2119 (13)	0.2214 (7)	42 (8)	70 (10)	63 (9)	9 (7)	5 (7)	10 (7)
C3	−0.2150 (10)	0.1271 (15)	0.3056 (6)	56 (9)	38 (9)	28 (8)	5 (8)	19 (8)	4 (7)
C4	−0.1295 (12)	0.1818 (14)	0.3646 (7)	86 (11)	77 (12)	24 (8)	−27 (8)	−4 (8)	−7 (8)
C5	−0.1180 (14)	0.1280 (20)	0.4394 (8)	128 (14)	110 (13)	27 (10)	−57 (12)	−23 (9)	0 (9)
C6	−0.1876 (14)	0.0198 (17)	0.4563 (8)	83 (11)	66 (12)	50 (11)	−22 (9)	9 (9)	3 (8)
C7	−0.2678 (11)	−0.0384 (13)	0.3982 (10)	48 (9)	56 (10)	64 (11)	−8 (7)	14 (8)	−1 (9)
C8	−0.2814 (10)	0.0168 (15)	0.3221 (7)	53 (9)	44 (10)	34 (10)	−7 (7)	0 (7)	11 (7)
C9	−0.2416 (11)	0.0863 (11)	0.0874 (6)	52 (8)	18 (8)	44 (9)	−13 (7)	15 (8)	−8 (6)
C10	−0.3386 (11)	0.0875 (14)	0.0249 (9)	69 (10)	59 (11)	43 (9)	−2 (8)	−2 (8)	−9 (8)
C11	−0.3320 (14)	0.0112 (16)	−0.0429 (9)	77 (12)	86 (13)	48 (11)	−7 (10)	−16 (9)	−11 (9)
C12	−0.2346 (16)	−0.0646 (16)	−0.0475 (9)	76 (13)	72 (12)	86 (14)	4 (10)	23 (11)	−26 (9)
C13	−0.1430 (12)	−0.0671 (14)	0.0131 (11)	64 (11)	71 (11)	91 (13)	11 (9)	33 (10)	−29 (10)
C14	−0.1437 (11)	0.0063 (14)	0.0804 (8)	63 (10)	55 (10)	64 (11)	18 (9)	14 (7)	−9 (8)
C15	−0.2823 (11)	0.4288 (12)	0.1666 (6)	45 (8)	20 (8)	38 (8)	−9 (7)	13 (7)	−6 (6)
C16	−0.3869 (10)	0.4676 (14)	0.1149 (7)	43 (9)	47 (12)	32 (8)	3 (7)	−3 (7)	−2 (6)
C17	−0.4107 (11)	0.6082 (16)	0.0957 (7)	73 (10)	38 (12)	45 (8)	11 (9)	3 (7)	12 (8)
C18	−0.3339 (14)	0.7134 (15)	0.1254 (8)	78 (11)	42 (10)	66 (10)	2 (9)	8 (9)	4 (8)
C19	−0.2286 (14)	0.6735 (16)	0.1766 (8)	92 (13)	63 (15)	67 (11)	−28 (10)	28 (10)	−23 (9)
C20	−0.2034 (11)	0.5322 (15)	0.1981 (7)	72 (10)	20 (10)	49 (9)	−8 (9)	6 (7)	4 (7)

squares refinement was done on F^2 in three stages: (A) scale, positional, and isotropic thermal parameters; (B) scale, positional, anisotropic Sb, and methoxyl group(s) with phenyl carbons isotropic (phenyl hydrogen contributions included); (C) final refinements allowed all atoms anisotropic thermal parameters (hydrogens fixed at a distance 1.08 Å from the carbon positions resulting from the isotropic refinement). The agreement factors at each stage are summarized in Table II. The final fractional coordinates and thermal parameters from the least-squares refinement, together with their standard deviations, are listed in Tables III and IV. The observed and calculated structure amplitudes F_o and F_c are available upon request.[17]

Results and Discussion

Methoxytetraphenylantimony. The crystal structure described by the space group, the parameters of Table III, and cell parameters consists of the packing of individual, monomeric molecules, as shown in Figure 1. The molecular structure (Figure 2) is that of a trigonal bipyramid with the oxygen atom and a carbon atom of

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(17) The tables of observed and calculated structure amplitudes have been submitted with the manuscript and have been deposited with the U.S. Library of Congress as Document No. 9719. Requests for copies should be adressed to: Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Photoduplication Service, Library of Congress.

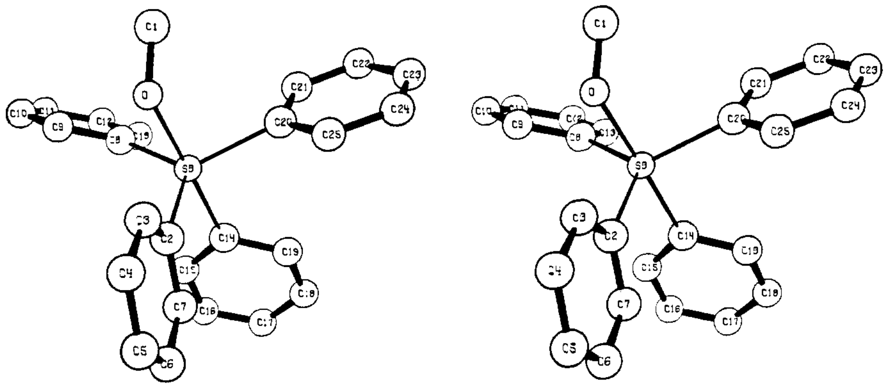

Figure 1. The molecular structure of $(C_6H_5)_4SbOCH_3$. This and subsequent figures are stereo pairs and may be conveniently viewed with the aid of a hand-held stereo viewer.

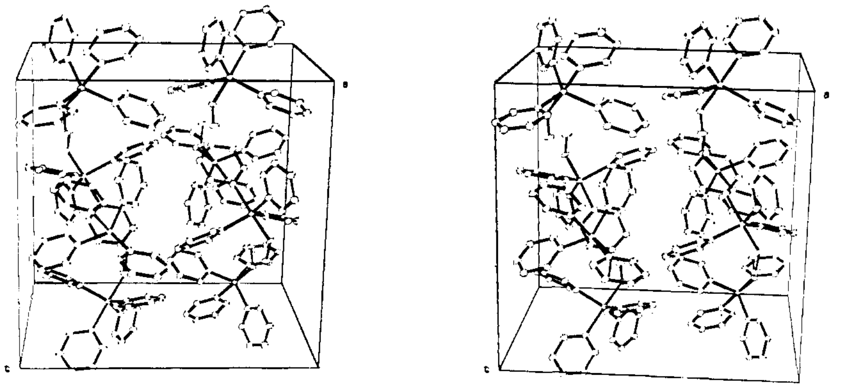

Figure 2. The molecular packing in the orthorhombic cell of $(C_6H_5)_4SbOCH_3$.

Table V. Intramolecular Angles and Distances for $(C_6H_5)_4SbOCH_3$

Intramolecular angle, deg						Intramolecular distance, Å			
O–Sb–C14	178.1 (5)	C3–C4–C5	117.9 (1.2)	C14–C15–C16	122.9 (1.4)	Sb–O	2.061 (7)	C11–C12	1.369 (19)
O–Sb–C2	85.1 (5)	C4–C5–C6	121.4 (1.3)	C15–C16–C17	120.6 (1.5)	Sb–C2	2.131 (11)	C12–C13	1.366 (19)
O–Sb–C8	87.2 (4)	C5–C6–C7	117.7 (1.2)	C16–C17–C18	119.0 (1.5)	Sb-C8	2.128 (13)	C13–C8	1.377 (17)
O–Sb–C20	89.5 (4)	C6–C7–C2	122.6 (1.3)	C17–C18–C19	120.4 (1.4)	Sb–C14	2.199 (14)	C14–C15	1.393 (17)
C2–Sb–C14	94.4 (5)	Sb–C8–C9	121.9 (8)	C18–C19–C14	120.7 (1.3)	Sb–C20	2.097 (15)	C15–C16	1.363 (19)
C8–Sb–C14	91.6 (5)	Sb–C8–C13	120.0 (8)	Sb–C20–C21	121.8 (1.4)	O–C1	1.395 (13)	C16–C17	1.362 (20)
C20–Sb–C14	92.3 (5)	C9–C8–C13	118.0 (1.0)	Sb–C20–C25	119.4 (1.4)	C2–C3	1.375 (14)	C17–C18	1.384 (20)
C2–Sb–C8	123.5 (4)	C8–C9–C10	119.2 (1.1)	C21–C20–C25	118.4 (1.3)	C3–C4	1.369 (15)	C18–C19	1.368 (18)
C2–Sb–C20	115.8 (6)	C9–C10–C11	122.0 (1.1)	C20–C21–C22	121.5 (1.5)	C4–C5	1.429 (18)	C19–C14	1.410 (18)
C20–Sb–C8	120.0 (6)	C10–C11–C12	119.0 (1.2)	C21–C22–C23	119.6 (1.6)	C5–C6	1.365 (15)	C20–C21	1.340 (19)
Sb–O–Cl	120.8 (7)	C11–C12–C13	119.3 (1.2)	C22–C23–C24	118.8 (1.8)	C6–C7	1.393 (15)	C21–C22	1.398 (20)
Sb–C2–C3	122.3 (1.0)	C12–C13–C8	122.5 (1.1)	C23–C24–C25	122.5 (1.8)	C7–C2	1.385 (15)	C22–C23	1.382 (22)
Sb–C2–C7	119.8 (1.2)	Sb–C14–C15	122.0 (1.2)	C24–C25–C20	119.1 (1.5)	C8–C9	1.386 (17)	C23–C24	1.294 (22)
C3–C2–C7	117.8 (1.2)	Sb–C14–C19	121.5 (1.2)			C9–C10	1.388 (19)	C24–C25	1.431 (22)
C2–C3–C4	122.5 (1.2)	C15–C14–C19	116.4 (1.2)			C10–C11	1.365 (20)	C25–C20	1.355 (18)

one benzene ring occupying the apical positions. The angle O–Sb–C_{14} is nearly ideal being 178.1° (5). The Sb, C_2, C_8, C_{20} atoms are approximately coplanar; the best least-squares plane[18] through these four atoms has the equation $7.843X - 8.035Y + 11.746Z + 0.184 = 0$ (crystal coordinates). The distances of these atoms from this plane are −0.0018 (8) Å for Sb, 0.165 (16) Å for C_2, 0.070 (11) Å for C_8, and 0.065 (11) Å for C_{20}. The fact that Sb is displaced out of the plane of C_2, C_8, C_{20} toward the apical phenyl group is probably due to steric interactions among the bulky benzene rings. Intramolecular distances and angles are given in Table V. The basal Sb–C bond distances of 2.131, 2.128, and 2.097 Å, and 2.119, 2.121, 2.119 Å for the dimethoxy derivative, described below, are significantly shorter than the apical Sb–C bond distance, 2.199 Å. This result is in agreement with the generally accepted rule that the more electronegative substituents always occupy the apical position and that this bond distance is always greater than the equatorial one. Although there have been many attempts to rationalize these facts for various kinds of pentavalent compounds,[19–21] the explana-

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[18] W. C. Hamilton, *Acta Cryst.*, 14, 185 (1965).

[19] R. J. Gillespie, *Inorg. Chem.*, 5, 1634 (1966).

[20] L. S. Bartell, *ibid.*, 5, 1635 (1966).

[21] P. C. Van Der Voorn and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3255 (1966).

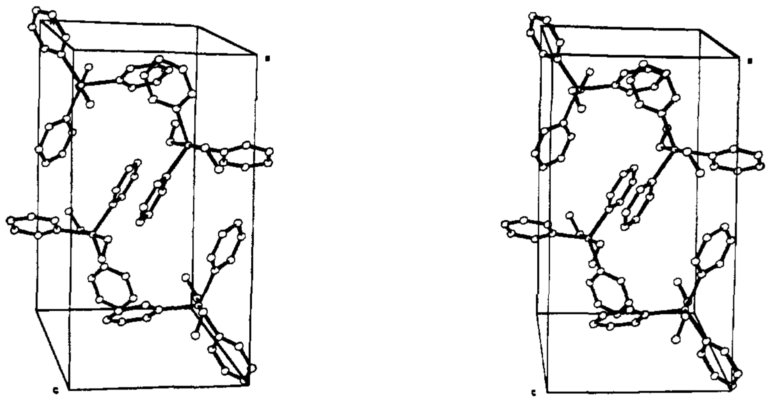

Figure 3. The molecular packing in the monoclinic cell of $(C_6H_5)_3Sb(OCH_3)_2$.

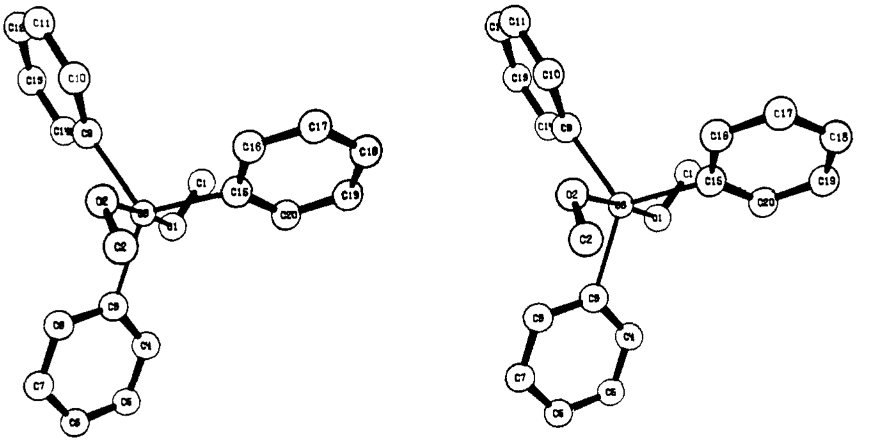

Figure 4. The molecular structure of $(C_6H_5)_3Sb(OCH_3)_2$.

tions are still considered to be controversial.[22] However, based on the difference in bond distances our expectation is that the apical Sb–C bond will have a higher chemical reactivity than the basal Sb–C bonds.

An extremely short nonbonded distance of 2.20 Å exists[23] between the phenyl proton associated with C_3 and the methoxyl oxygen atom. With the aid of Figure 1 viewed stereoscopically, the "pseudo" planar five-membered ring formed by C_3, C_2, Sb, O, and H of C_3 (not shown) can easily be visualized. The 2.06-Å Sb–O distance[24] along with the chemical and other physical properties of I[2] indicate that the Sb–O bond has little ionic character. For example, the melting point of the compound is 132°, it is readily soluble in petroleum ether, and its nmr spectrum shows a singlet absorption peak at δ 2.74 ppm relative to TMS for the methoxyl group.[25] The fact that a trigonal bipyramidal configuration is adopted in the crystalline state does not prove that the same holds true in solution. The energy of activation required to interconvert the trigonal bipyramid and the square pyramid should be small; thus, an equilibrium may exist between these two states in solution.[3,22,26] Methoxytetra-*p*-tolylantimony ($(p\text{-}CH_3C_6H_4)_4SbOCH_3$) has been synthesized, and the nmr spectrum of this compound exhibits only a single sharp peak at δ 2.35 ppm for the *p*-methyl protons even at −60°. This result suggests that this compound exists in solution either as a rapidly established equilibrium mixture of trigonal-bipyramidal and square-pyramidal configurations or as the latter configuration only.[27] Tracer studies and dipole moment measurements presently under investigation hopefully will shed further light on the stereochemistry of these and other organoantimony(V) compounds in solution.

Dimethoxytriphenylantimony. The crystal structure described by the space group, the parameters of Table IV, and cell parameters indicates the packing of monomeric molecules containing pentacoordinated Sb atoms (Figure 3). The molecular structure, shown in Figure 4, is a trigonal bipyramid with two oxygen atoms occupying the apical positions and with the benzene ring carbon atoms in the basal plane. The intramolecular bond distances and angles are given in Table VI. The

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[22] For a brief discussion of this problem, see E. L. Muetterties, *Inorg. Chem.*, **6**, 635 (1967).

[23] Assumes van der Waals radii of 1.2 Å for H and 1.4 Å for O: L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

[24] L. Pauling, ref 23, p 224. The covalent radii for Sb and O are given as 1.41 and 0.66 Å, respectively.

[25] The fact that the nmr methoxyl peak is absent in a methanol solution of I can be attributed to rapid exchange of solvent molecules with the methoxyl group bonded to antimony.[2] This does not negate the statement that the Sb–O bond is covalent in the crystalline state, for the strongly solvating power of methanol is sufficient to cause the exchange.

[26] D. Hellwinkel [*Angew. Chem. Intern. Ed. Engl.*, **5**, 725 (1966)] has suggested that pentaphenylantimony in solution might undergo rapid transformation between the two states of pentaphenylantimony.

[27] There is no evidence presently available to indicate whether the methyl hydrogen atoms of a *p*-tolyl group located in a basal position of a trigonal bipyramidal molecule will have a different chemical shift in the nmr spectrum from the methyl hydrogens of a *p*-tolyl group located in an apical position. Experiments designed to clarify this point are presently in progress.

Table VI. Intramolecular Angles and Distances for $(C_6H_5)_3Sb(OCH_3)_2$

Intramolecular angle, deg						Intramolecular distance, A			
O1–Sb–O2	175.3 (3)	Sb–C3–C4	121.5 (1.1)	C10–C11–C12	120.9 (8)	Sb–O1	2.039 (8)	C9–C10	1.388 (14)
C3–Sb–C9	124.0 (5)	Sb–C3–C8	119.7 (9)	C11–C12–C13	120.1 (1.3)	Sb–O2	2.027 (8)	C10–C11	1.390 (18)
C3–Sb–C15	121.4 (5)	C4–C3–C8	118.8 (1.0)	C12–C13–C14	121.8 (1.2)	O1–O1	1.429 (12)	C11–C12	1.344 (16)
C9–Sb–C15	114.6 (4)	C3–C4–C5	118.9 (1.2)	C13–C14–C9	120.1 (1.1)	O2–C2	1.411 (13)	C12–C13	1.327 (16)
O1–Sb–C3	85.5 (4)	C4–C5–C6	122.0 (1.1)	Sb–C15–C16	119.4 (9)	Sb–C3	2.119 (10)	C13–C14	1.355 (16)
O1–Sb–C9	93.4 (4)	C5–C6–C7	119.4 (1.2)	Sb–C15–C20	121.4 (9)	Sb–C9	2.121 (11)	C14–C9	1.380 (14)
O1–Sb–C15	92.2 (4)	C6–C7–C8	119.1 (1.1)	C16–C15–C20	119.2 (1.0)	Sb–C15	2.119 (12)	C15–C16	1.395 (14)
O2–Sb–C3	91.5 (4)	C7–C8–C3	121.7 (1.0)	C15–C16–C17	120.6 (1.0)	C3–C4	1.366 (14)	C16–C17	1.376 (15)
O2–Sb–C9	85.6 (4)	Sb–C9–C10	119.8 (1.0)	C16–C17–C18	121.8 (1.1)	C4–C5	1.371 (16)	C17–C18	1.356 (16)
O2-Sb–C15	92.1 (4)	Sb–C9–C14	121.6 (1.0)	C17–C18–C19	117.3 (1.2)	C5–C6	1.363 (17)	C18–C19	1.399 (17)
Sb–O1–C1	122.5 (6)	C10–C9–C14	118.5 (1.0)	C18–C19–C20	122.1 (1.1)	C6–C7	1.335 (16)	C19–C20	1.394 (17)
Sb–O2–C2	120.7 (6)	C9–C10–C11	118.7 (1.1)	C19–C20–C15	119.1 (1.1)	C7–C8	1.395 (15)	C20–C15	1.366 (14)
						C8–C3	1.353 (14)		

Table VII. Phenyl Group Least-Squares Planes[a]

Carbon atom nos. in plane	A	B	C	D
		Compound I		
2–7	7.514	14.437	1.527	3.873
8–13	2.837	3.158	16.132	1.750
14–19	10.760	−4.643	−10.538	−0.250
20–25	6.256	−6.683	13.647	0.250
		Compound II		
3–8	8.408	−6.145	−5.919	−4.382
9–14	5.448	7.478	−8.078	−1.382
15–20	7.204	−0.924	−15.312	−4.982

[a] Of the form $Ax + By + Cz - D = 0$ where x, y, and z are the fractional coordinates of the atoms.

Sb, C_3, C_9, and C_{15} atoms are coplanar; the best least-squares plane through these four atoms has the equation $11.251X + 1.731Y - 1.701Z + 2.709 = 0$, and the atomic displacements from this plane are 0.0001 (7) Å for Sb and −0.01 (1) Å for C_3, C_9, and C_{15}. The slight distortion of the O_1–Sb–O_2 angle to 175.3 (3)° may plausibly be the result of packing requirements; *i.e.*, the six oxygen nearest *o*-phenyl hydrogen contacts are at distances which range from 2.45 to 2.67 Å. The coefficients of the least-squares plane through the carbon atoms for each phenyl ring of both compounds are listed in Table VII. The maximum displacement from these planes is 0.018 (18) Å, with the average being about half this value. The nmr spectrum[2] of this compound is in agreement with the molecular structure determined here.

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Stereoselectivity in the Metal-Complex-Catalyzed Hydrolysis of Amino Acid Esters[1a]

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Abstract: The hydrolysis of (*R*)-(−)- and (*S*)-(+)-histidine methyl esters in the presence of the catalytically active complexes Ni((*R*)-(−)-histidinate)$^+$ and Ni((*S*)-(+)-histidinate)$^+$ has been examined in detail. The rate of hydrolysis of the (*R*)-(−) ester is greater in the presence of the Ni((*S*)-(+)-histidinate)$^+$ ion than in the presence of Ni((*R*)-(+)-histidinate)$^+$, and these rate differences are mirrored in the behavior of the (*S*)-(+) ester. The system with opposite ester–histidine configurations has an observed rate constant approximately 40% greater than that found with identical ester–histidine configurations. A more detailed evaluation of the experimental data indicates that the stereoselectivity results from differences in the specific rates of hydrolysis for the coordinated ligands, arising from differences in the degree of interaction between the ester carbonyl group and the coordination center. Differences in the stability constants of the species involved are not believed to play an important role in the stereoselectivity.

It has previously been shown in various studies that several metal ions and their complexes are effective catalysts for the hydrolysis of amino acid esters.[2–6] In these instances, coordination of the ester to a metal ion makes it more susceptible to attack by the nucleo-

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