Molecular Structure of Tetraphenylantimony Hydroxide[1]

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Abstract: The structure of tetraphenylantimony hydroxide has been determined from three-dimensional X-ray diffraction data (1912 independent reflections) measured on a counter diffractometer. The molecule is a slightly distorted trigonal bipyramid with the hydroxyl group occupying an axial position. The antimony–carbon bond lengths are 2.218 Å for the axial bond and in the range 2.116–2.140 Å for the equatorial bonds while the antimony–oxygen distance is 2.048 Å. The molecules are packed in pairs with the –OH groups facing each other through the center of symmetry and associated by hydrogen bonding. Pertinent crystallographic data are as follows: space group, P$\bar{1}$, unit cell dimensions, $a = 10.309 \pm 0.007$ Å, $b = 10.138 \pm 0.007$ Å, $c = 10.373 \pm 0.007$ Å; $\alpha = 92° 3' \pm 3'$; $\beta = 86° 3' \pm 3'$; $\gamma = 112° 35' \pm 3'$; $V = 998.6$ Å^3; density 1.50 ± 0.01 g cm^{-3} (measured), 1.49 g cm^{-3} (calcd for $Z = 2$).

The preparation of tetraphenylantimony hydroxide was described a few years ago.[3] Its properties differ markedly from those of the quaternary hydroxides of the lighter elements of group Vb and might suggest a nonionic structure in the solid state. Indeed, unlike the substituted ammonium, phosphonium, and arsonium hydroxides which behave in many respects as alkali metal hydroxides and can only be isolated as hydrated solids or syrupy liquids which are unstable when approaching the anhydrous state,[4] tetraphenylantimony hydroxide was reported to exist as a slightly water-soluble, anhydrous solid and to remain unchanged upon exposure to carbon dioxide.[5]

An X-ray structure investigation of this compound appeared desirable for several reasons. It is an AB$_4$M type of potentially pentacoordinate molecule that might differ from pentaphenylantimony only by substitution of one phenyl ring; the latter molecule is the only group Vb pentacoordinate species (without lone pair) which does not have a trigonal-bipyramidal structure.[6,7] At the inception of the present work, no AB$_4$M compound of antimony had been subjected to X-ray investigation. The methoxytetraphenylantimony molecule has recently been reported to be trigonal bipyramidal with the methoxy group at an axial position.[8] Furthermore, the ready interconvertibility of the oxide, $[(C_6H_5)_4As]_2O$, and the hydroxide in aqueous media leaves open the *a priori* possibility of a formulation like $[(C_6H_5)_4Sb]_2O \cdot H_2O$ for the hydroxide. Its infrared spectrum shows two bands in the –OH stretching frequency range, one of which seems to correspond to a similar band for the hydroxides $(C_6H_5)_3MOH$ of silicon, germanium, tin, and lead.[9] Controversy arose about the assignment of this band,[10] and no definitive explanation has been given yet.

The results of a three-dimensional X-ray structure determination of tetraphenylantimony hydroxide are reported here. It is found that the molecule is trigonal bipyramidal, with the OH group in an axial position.

Experimental Section

Preparation. Tetraphenylantimony hydroxide was prepared by addition of ammonium hydroxide to an aqueous solution of tetraphenylantimony bromide (Alfa Inorganics) and purified as described by Affsprung and May.[5] It was dried under vacuum at room temperature. Crystals suitable for X-ray work were grown by interdiffusion of water and a solution of the compound in a 1:3 water:acetone mixture. These crystals lose water and become opaque at 105–110°, begin to decompose slowly at about 165°, and melt at 213–214° (lit.[5] 213–217°); these temperatures are dependent on the rate of heating.

Anal. Calcd for $C_{24}H_{21}OSb$: C, 64.46; H, 4.73; basic equiv wt, 447.2. Found: C, 64.53; H, 4.73; basic equiv wt (by dissolution in slight excess of H_2SO_4 and back-titration with NaOH), 448 ± 2.

Attempts to recrystallize the hydroxide from hot aqueous methanol yielded a colorless solid that remained unchanged on heating at 105–110° but behaved like the hydroxide upon further increase of temperature. The infrared spectrum shows that this compound is identical with the one obtained by heating the hydroxide at 105–110°, which is reported[3] to be the oxide, $[(C_6H_5)_4Sb]_2O$. The analysis is consistent with this formulation. The hydroxide can be regenerated by dissolving the oxide in dilute H_2SO_4 and adding ammonium hydroxide.

Anal. Calcd for $C_{48}H_{40}OSb_2$: C, 65.79; H, 4.60; basic equiv wt, 438.2. Found: C, 65.58; H, 4.68; basic equiv wt, 436 ± 2.

Data Collection. The crystals grown from acetone–water mixtures as described above are triclinic parallelepipeds elongated along the *a* axis. The compound is not air sensitive and all the X-ray work was carried out on crystals exposed to the atmosphere.

Weissenberg (0*kl*, 1*kl*) and precession photographs (*h*0*l*, *h*1*l*, *h*2*l*, *hk*0, *hk*1, *hk*2) indicated one of the triclinic space groups P1 or P$\bar{1}$. The unit cell constants were obtained at 23° by a linear extrapolation procedure previously explained,[11] with 2θ values measured on a General Electric XRD-5 manual single-crystal diffractometer, using Cu Kα radiation ($\lambda(K\alpha_1)$ 1.5405 Å, $\lambda(K\alpha_2)$ 1.5443 Å); $a = 10.312 \pm 0.007$ Å, $b = 10.140 \pm 0.007$ Å, $c = 10.364 \pm 0.007$ Å; $\alpha = 92° 3' \pm 3'$, $\beta = 86° 3' \pm 3'$, $\gamma = 112°$

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[1] Research supported by the National Science Foundation, under Grant No. GP 7034X.

[2] Hydro-Quebec Postdoctoral Fellow, 1966–1968.

[3] K. D. Moffett, J. R. Simmler, and H. A. Potratz, *Anal. Chem.*, **28**, 1356 (1956).

[4] (a) G. E. Razuvaev, V. S. Malinovskii, and D. A. Godina, *J. Gen. Chem. USSR*, **5**, 721 (1935); *Chem. Abstr.*, **30**, 1057 (1936); (b) P. Pascal, Ed., "Nouveau Traité de Chimie Minérale," Masson & Cie, Editeurs, Paris, Vol. X, 1965, p 938; Vol. XI, 1965, p 414; (c) D. L. Fowler, W. V. Loebenstein, D. B. Paul, and C. A. Kraus, *J. Am. Chem. Soc.*, **62**, 1140 (1940); (d) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. Van der Werf, *ibid.*, **86**, 2378 (1964), and references therein.

[5] H. E. Affsprung and H. E. May, *Anal. Chem.*, **32**, 1164 (1960).

[6] P. J. Wheatley, *J. Chem. Soc.*, 3718 (1964).

[7] A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6675 (1968).

[8] K. Shen, W. E. McEwen, S. J. LaPlaca, W. C. Hamilton, and A. P. Wolf, *ibid.*, **90**, 1718 (1968).

[9] R. West and R. H. Baney, *J. Phys. Chem.*, **64**, 822 (1960).

[10] B. Kushlefsky, I. Simmons, and A. Ross, *Inorg. Chem.*, **2**, 187 (1963).

[11] M. J. Bennett, F. A. Cotton, and J. Takats, *J. Am. Chem. Soc.*, **90**, 903 (1968).

34′ ± 3′. The observed density obtained by flotation in aqueous KI solutions (1.50 ± 0.01 g cm^{-3}) agrees well with the calculated value of 1.487 from the formula weight 447.2, $Z = 2$, and unit cell volume of 998.6 $Å^3$.

Periodic checks of four reflections (020, 050, $00\bar{3}$, and 410) indicated a slow decomposition of the crystal in the X-ray beam. Hence two crystals (0.23 × 0.19 × 0.30 mm and 0.14 × 0.10 × 0.17 mm) were used to collect intensity data. Each was discarded when the intensity of the 050 standard reflection had fallen by 15%. The crystals were mounted with their a^* axes coincident with the ϕ axis of the General Electric XRD-5 diffractometer. The distances from the crystal to the source and from the crystal to the circular aperture (2°) at the counter were 5.73 and 7.05 in., respectively. The intensities were measured with a scintillation counter with pulse-height discriminator set to receive 95% of the nickel-filtered Cu Kα radiation with the window centered on the Cu Kα peak. A $\theta/2\theta$ scan technique was employed at a 2θ scan rate of 4°/min. The peak counts, P, were obtained from a 2θ scan of 2.66° from $2\theta_{\text{calcd}} - 1.33°$ to $2\theta_{\text{calcd}} + 1.33°$. Stationary background counts, B_1 and B_2, of 20 sec each were taken at each of the limits of the scan. The integrated intensities, I, were then obtained from the expression $I = P - (B_1 + B_2)$.

The integrated intensities of 2095 independent reflections within a sphere $2\theta \leq 50.5°$ were measured using Ni-filtered Cu Kα radiation. Statistically insignificant reflections (183) were rejected using the two criteria: (1) $I \leq 0$; (2) $I < 3(P + B_1 + B_2)^{1/2}$. A correction for decomposition was then applied. The intensity I_t, measured at time t, was reduced to the hypothetical intensity I_0 of the non-decomposed crystal using an equation of the form $I_0 = I_t \exp(kt \sin^2 \theta/\lambda^2)$. The decay constant, k, obtained from the lines ln I_t *vs.* time corresponding to the standard reflections checked every 4 hr, was found equal to 0.072 hr^{-1} for both crystals. The correction was found satisfactory for the 23 duplicate reflections measured both at the beginning and at the end of the data collection and covering the entire range of sin θ/λ values. The intensities I_0 were then corrected for the Lorentz and polarization effects.

The $h00$ reflections were found to show significant variations in intensity as a function of the orientation of the crystals; ϕ scans of several of them indicated variations of ±15% for both crystals. An absorption correction ($\mu = 109.2$ cm^{-1}) based on the equations of the crystal faces was applied in the later stage of the refinement. The transmission factors were in the range 0.15–0.20 and 0.30–0.38 for crystal no. 1 and crystal no. 2, respectively. The variations on ϕ scans were reduced to ±8% after absorption corrections were applied.

Solution and Refinement of the Structure

A three-dimensional Patterson map readily revealed the positions of all atoms except hydrogen. The locations of the carbon and oxygen atoms suggested the choice of space group $P\bar{1}$ which was confirmed by subsequent successful refinement.

The structure was refined by the conventional least-squares method. For atoms other than hydrogen the scattering factors were those of Cromer and Waber,[12] while the form factors used for hydrogen were those experimentally determined by Mason and Robertson.[13] The anomalous dispersion contributions for antimony ($\Delta f' = -0.9$ e, $\Delta f'' = 6.10$ e) were included in the calculation of structure factors.[14] The function minimized during the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ is the observed structure amplitude, $|F_c|$ is the calculated amplitude, and w is a weighting factor. A number of computer programs were used at this and other stages of the solution and refinement of the structure.[15]

Seven cycles of full-matrix refinement of scale factors and positional and isotropic temperature factors of all atoms except hydrogen led to a discrepancy index $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.055$ and a weighted residual $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2} = 0.072$. The antimony atom was assigned an anisotropic temperature factor $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and two cycles of refinement of scale factors and all parameters for antimony, carbon, and oxygen atoms resulted in $R_1 = 0.051$ and $R_2 = 0.069$. A difference Fourier map using all data revealed the positions of all phenyl hydrogen atoms. In the next cycle, an anisotropic temperature factor was assigned to the oxygen atom. All parameters previously mentioned were varied, together with the coordinates and isotropic temperature factors of the 20 phenyl hydrogen atoms. These parameters for 15 of the hydrogen atoms were found to refine reasonably well, but the remaining five showed negative or very high temperature factors. Each of them was fixed at a distance of 1.08 Å from the corresponding carbon atom and one more cycle led to $R_1 = 0.048$ and $R_2 = 0.065$. It was then realized that the absorption coefficient μ used in the computation of the absorption correction was slightly in error. A new absorption correction was calculated using $\mu = 109.2$ cm^{-1}. At this point, a program[7] for the least-squares refinement of phenyl rings as rigid bodies became available and was used for the final stage of refinement. The rigid body parameters were generated from the positional coordinates of the carbon atoms obtained in the previous cycle, assuming an ideal distance of 1.397 Å from the center of gravity of the ring to each carbon atom. The hydrogen atoms were fixed at the calculated distance (1.08 Å) from the carbon atoms and shifted after each cycle in accordance with the shifts of the carbon atoms. Five cycles of refinement of scale factors, coordinates, and anisotropic temperature factors of the antimony and oxygen atoms and coordinates and isotropic temperature factors of four phenyl rigid bodies resulted in convergence with $R_1 = 0.049$ and $R_2 = 0.062$. The hydrogen atoms were assigned isotropic temperature factors equal to 1.1 times those of the carbon atoms to which they are attached. In the last cycles, two of the rotation coordinates (E and F) for rigid body no. 3 came out with high estimated standard deviations. Inspection of the correlation matrix revealed that for these particular values the coordinates E and F are degenerate and lead to a near singular matrix (correlation coefficient, −0.99). This situation has been described by J. A. Ibers in the Brookhaven crystallographic program manual and the possible solutions are (1) to redefine the internal Cartesian coordinate system or (2) to fix one of the angles. It was simpler to do the latter. This did not change the values of the other parameters previously obtained by more than one-third of their estimated standard deviations but

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(12) D. T. Cromer and J. T. Waber, *Acta Cryst.*, 18, 104 (1965).

(13) R. Mason and G. B. Robertson in "Advances in Structure Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience Division, John Wiley & Sons, New York, N. Y., 1966, p 57.

(14) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1965, p 215.

(15) Computer programs for the IBM 360 computer used in this study were: D. P. Shoemaker, MIXG2 (calculates diffractometer settings) and DISTAN (orthogonal cell coordinates, inter- and intramolecular contacts and angles); R. C. Elder, PDATA2 (corrects MIGX2 output for ϕ_0 and scan width and prints diffractometer settings in convenient format) and PUBTAB (prepares structure factors in proper format for publication); W. C. Hamilton, GONO9 (used for absorption correction); A. Zalkin, FORDAP (Fourier summation for Patterson or difference Fourier maps); C. T. Prewitt, SFLS5 (least-squares refinement of parameters) and SFLS5R (with rigid body routine, adapted by M. J. Bennett and B. M. Foxman); M. J. Bennett, PMMO (general data reduction program); J. S. Wood, MGEOM (bond lengths and angles with standard deviations and best least-squares planes).

Table I

A. Positional Parameters[a] for Sb and O

	x	y	z
Sb	0.23748 (5)	0.10660 (5)	0.16937 (5)
O	0.0370 (6)	0.0664 (7)	0.1192 (7)

B. Anisotropic and Equivalent Isotropic Temperature Parameters[a,b] for Sb and O

Sb	9.11 (9), 9.81 (8), 7.09 (8), 3.65 (6), −0.80 (7), −0.41 (5); equivalent B = 3.25 Å^2
O	8.2 (8), 21.7 (10), 18.2 (10), 6.0 (7), −1.7 (7), 4.6 (8); equivalent B = 6.02

[a] Standard deviations occurring in last quoted figure are given in parentheses. [b] Anisotropic tensor components ($\times 10^3$) given in the order $\beta_{11}, \beta_{22}, \beta_{33}, \beta_{12}, \beta_{13}, \beta_{23}$.

Table II. Rigid Body Coordinates[a,b]

Body	x	y	z	D	E	F
C_{11}–C_{16}	0.1582 (4)	−0.2647 (4)	0.1722 (4)	0.0654 (37)	2.8736 (38)	1.7696 (68)
C_{21}–C_{26}	0.3317 (4)	0.2495 (4)	−0.1424 (4)	0.1705 (41)	1.3993 (38)	3.4480 (32)
C_{31}–C_{36}	0.5919 (5)	0.2024 (4)	0.2683 (4)	4.8795 (35)	0.5078[c]	2.2716[c]
C_{41}–C_{46}	0.1631 (5)	0.3109 (5)	0.4258 (5)	0.6443 (46)	0.4936 (60)	5.2298 (52)

[a] Standard deviations in the last quoted figure are given in parentheses. [b] For the sets of H atoms, H_{i2}–H_{i6}, x, y, z, D, and E are identical with those for the corresponding sets of C atoms, C_{i2}–C_{i6}. F for an H atom set is equal to the F for the corresponding C atom set plus $2\pi/6$ radians since there is no H on C_{i1} and the H atom set begins with H_{i2}. [c] Because of the difficulty of degeneracy in E and F mentioned in the text, only the standard deviation for the sum of these, 0.0033 radian, could be determined.

yielded a reasonable value for the estimated standard deviation of coordinate E. It was also verified that the same results are obtained when E instead of F is not varied. A final difference Fourier map using all data showed no peak higher than 0.9 e Å^{-3}. Although weak peaks were observed in the region where the hydrogen atoms of the OH groups might be expected (at $x = -0.01$, $y = 0.03$, $z = 0.06$ and at $x = 0.03$, $y = 0.15$, $z = 0.12$), stronger peaks were obtained on the other side of the oxygen atom, so that unambiguous assignment of these peaks is not possible.

A table of the $|F_o|$ and final $|F_c|$ values has been prepared and deposited with the American Documentation Institute.[16]

Results

The molecular structure of tetraphenylantimony hydroxide is shown in Figure 1. The carbon and hydrogen atoms are labeled with double indices. The first index is the number of the ring, while the second gives the number of the atom within the ring, second index 1 denoting the carbon atom which is bound to the antimony atom.

Positional and anisotropic thermal parameters for the antimony and oxygen atoms are given in Table I. The rigid body coordinates[7] for the phenyl groups are given in Table II while Table III gives the positional coordinates for individual carbon atoms and their isotropic thermal parameters. Table IV gives molecular dimensions calculated from the data in Tables I and III. The carbon–carbon bond lengths, which were fixed at 1.397 Å, turned out to have standard deviations of 0.008 Å except for those in ring 4 where values of about 0.01 Å were found.

The equatorial C_{j1} atoms make contacts of 2.82–2.95 Å with the oxygen atom and of 3.10–3.20 Å with the axial (C_{31}) atom. Apart from distances across the phenyl rings, the only intramolecular contacts short enough to deserve mention involve oxygen and ring 1: O–C_{16}, 2.94 Å; O–H_{16}, 2.29 Å. Four C–H intermolecular contacts are found in the range 2.63–2.77 Å; these values are slightly but not unreasonably lower than the sum of the van der Waals radii (H, 1.2 Å, half-thickness of a benzene ring, 1.7 Å).

Discussion

While the tetraphenylantimony hydroxide molecule in its entirety has no symmetry, this is chiefly because of the varied orientations of the phenyl rings. The oxygen atom and the four carbon atoms which are attached to the antimony atom lie close to the vertices of a trigonal bipyramid with the antimony atom at its center, although there are definite distortions. Thus the average C(ax)–Sb–C(eq) angle is 93.4° and the average C(eq)–Sb–O angle is 86.7°, whereas all of these should be 90° in a perfect trigonal bipyramid. Since the two axial positions are occupied by different kinds of atoms, however, this sort of distortion is not in conflict with the best idealized symmetry possible for this molecule, *viz.*, C_{3v}. Even for this symmetry, the O–Sb–C(ax) angle should be 180°, whereas, in fact, an angle of 175.4° is found. Further, the three C(eq)–Sb–C(eq) angles should be 120°. The average value, 119.7°, is very close to this, but the individual angles lie in the range 114.0–123.9°. Nonetheless, it is reasonable to describe this structure as distorted trigonal

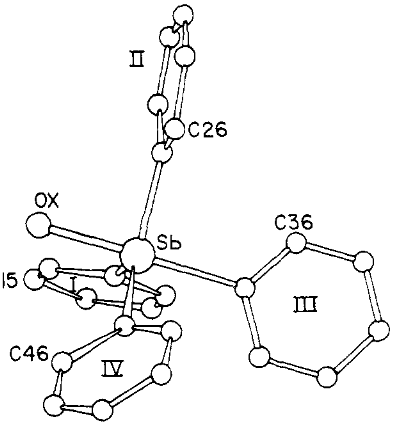

Figure 1. The $(C_6H_5)_4SbOH$ molecule as seen in a projection down the axis obtained upon rotating the b axis by 10° about the X axis (a sin γ) of an orthogonal coordinate system.

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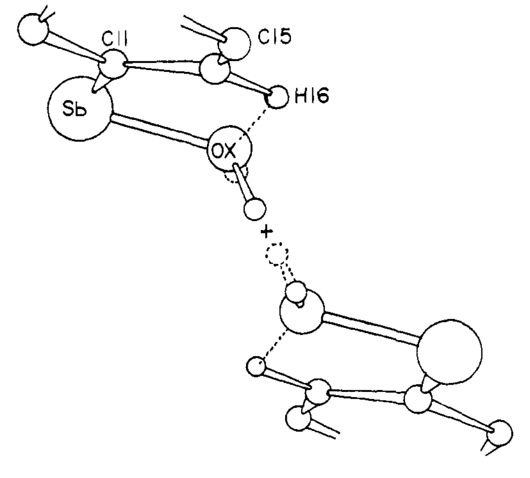

Figure 2. A detailed view of the intermolecular contact in the region of hydrogen bonding. The two equally probable sets of hydroxy hydrogen atoms are shown in full and broken lines. The + sign indicates a crystallographic center of symmetry.

bipyramidal. By no means could it be construed as a distorted square pyramid, and thus $(C_6H_5)_5Sb$ remains the only pentacoordinate molecule formed by a group V element with a ten-electron valence shell which is not trigonal bipyramidal.

Table III. Positional and Thermal Parameters[a] of Carbon Atoms

	x	*y*	*z*	*B*, Å^2 [b]
C11	0.1888 (6)	−0.1180 (5)	0.1740 (6)	3.7
C12	0.2934 (5)	−0.1683 (5)	0.1974 (4)	4.2
C13	0.2629 (5)	−0.3150 (6)	0.1956 (5)	5.5
C14	0.1278 (6)	−0.4114 (4)	0.1704 (6)	5.6
C15	0.0231 (5)	−0.3611 (5)	0.1470 (4)	5.5
C16	0.0536 (5)	−0.2143 (6)	0.1488 (5)	4.5
C21	0.3003 (7)	0.1964 (6)	−0.0168 (4)	3.3
C22	0.3023 (7)	0.1054 (4)	−0.1206 (6)	4.7
C23	0.3336 (7)	0.1586 (5)	−0.2463 (5)	6.0
C24	0.3630 (7)	0.3027 (6)	−0.2680 (4)	5.9
C25	0.3611 (7)	0.3936 (4)	−0.1642 (6)	6.1
C26	0.3297 (7)	0.3405 (6)	−0.0385 (5)	5.1
C31	0.4552 (6)	0.1668 (6)	0.2299 (5)	4.1
C32	0.4779 (8)	0.1541 (4)	0.3593 (4)	5.3
C33	0.6146 (5)	0.1896 (6)	0.3977 (5)	6.2
C34	0.7287 (6)	0.2379 (6)	0.3067 (5)	6.3
C35	0.7060 (8)	0.2507 (4)	0.1773 (4)	5.7
C36	0.5693 (5)	0.2152 (6)	0.1389 (5)	4.2
C41	0.1908 (9)	0.2258 (8)	0.3275 (8)	4.6
C42	0.2923 (6)	0.3604 (8)	0.3544 (6)	5.7
C43	0.2646 (7)	0.4455 (6)	0.4528 (6)	7.3
C44	0.1354 (9)	0.3960 (8)	0.5241 (8)	7.7
C45	0.0339 (6)	0.2614 (8)	0.4972 (6)	7.7
C46	0.0616 (7)	0.1764 (6)	0.3988 (6)	6.9

[a] Standard deviations occurring in last quoted figure are given in parentheses. [b] Standard deviations for all carbon atom *B*'s are approximately 0.2 Å^2.

Table IV. Bond Lengths (Å) and Bond Angles (degrees)[a]

Sb–C_{11}	2.136 (4)	C_{11}–Sb–O	89.6 (3)
Sb–C_{21}	2.116 (5)	C_{21}–Sb–O	85.3 (2)
Sb–C_{41}	2.140 (8)	C_{41}–Sb–O	85.3 (3)
Av Sb–C(eq)	2.131	Av O–Sb–C(eq)	86.7
Sb–C_{31}	2.218 (5)	C_{31}–Sb–O	175.4 (2)
C_{11}–Sb–C_{21}	114.0 (2)	C_{31}–Sb–C_{11}	94.5 (2)
C_{11}–Sb–C_{41}	123.9 (3)	C_{31}–Sb–C_{21}	94.7 (2)
C_{21}–Sb–C_{41}	121.2 (3)	C_{31}–Sb–C_{41}	90.9 (3)
Av C(eq)–Sb–C(eq)	119.7	Av C(ax)–Sb–C(eq)	93.4

[a] Standard deviations occurring in last quoted figure are given in parentheses.

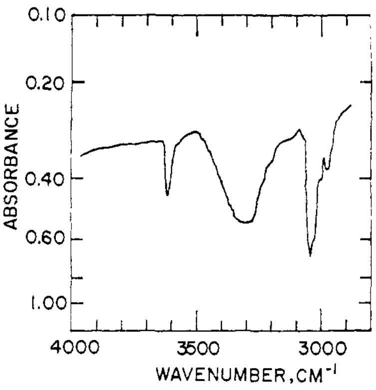

Figure 3. A portion of the infrared spectrum of crystalline $(C_6H_5)_4SbOH$ (hexachlorobutadiene mull; Perkin-Elmer grating spectrophotometer, Model No. 337).

Other features of this structure are consistent with the known properties of trigonal-bipyramidal molecules.[17] Thus the Sb–C(ax) bond is longer (by 0.09 Å) than the average Sb–C(eq) bond, and the more electronegative atom, oxygen, occupies an axial position. Sb–C bond lengths similar to those found here have been reported for other phenylantimony compounds[8,18] and the Sb–O distance is close to that found in tetraphenylantimony methoxide.[8]

The intermolecular arrangement in the crystal of tetraphenylantimony hydroxide is of distinct interest. The molecules occur in pairs (see Figure 2) with the oxygen atoms related to each other through the center of symmetry at the origin of the unit cell. A value of 2.78 Å for the oxygen–oxygen contact is less than that expected for two independent molecules but is comparable to that found for alcohols and phenols which are associated by hydrogen bonding in the solid state.[19] The Sb–O–O angle is equal to 116.5°. This is a suitable angle for an Sb–O–H group, so that a pair of molecules fulfills the obvious geometrical requirements for association *via* hydrogen bonding with the hydrogen atom lying on or close to the oxygen–oxygen line. While one hydrogen atom would actually be involved in the hydrogen bond, that of the opposite molecule would remain free and the center of symmetry should vanish when the hydroxylic protons are taken into account.

Such an effect would hardly be detectable experimentally and so cannot be ruled out, but it seems much more likely that the centric P$\bar{1}$ space group is retained as a result of disordering of the hydroxyl protons. Thus, between each pair of oxygen atoms there would be one proton (probably on two equivalent, off-center positions, each half-populated) while the free proton would be equally and randomly distributed over the two equivalent sites available to those protons not engaged in hydrogen bonding. With regard to the latter, it would appear that the short intramolecular O–H_{16} contact requires that it be directed away from ring 1. The appearance of weak peaks on the final difference Fourier map (at −0.01, 0.03, 0.12 and 0.03,

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(17) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

(18) T. N. Polynova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **7**, 642, 742 (1966).

(19) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., London, 1960, p 271.

0.15, 0.12) is consistent with the preceding discussion, but, because of the presence of other peaks about oxygen, some larger than those just mentioned, no more can be said on this basis.

The infrared spectrum supports the proposed hydrogen-bond arrangement. The 2800–4000-cm^{-1} portion of the infrared spectrum of solid tetraphenylantimony hydroxide is given in Figure 3. Two bands are observed in the OH stretching region: a broad band at $\sim$3320 cm^{-1}, whose shape and relatively low wave number indicate a hydrogen-bonded OH group, and a sharp peak at 3620 cm^{-1} which corresponds to a free OH group. Sharp peaks in the range 3609–3677 cm^{-1} have been reported for dilute solutions of $(C_6H_5)_3MOH$ compounds of group IVb elements in nonpolar solvents, where no association of any sort is believed to occur.[9] Although the assignment of this band has been questioned for $(C_6H_5)_3SnOH$,[10] the present results definitely support the assignment of the higher wave number sharp peak to the free hydroxyl group. In addition to these bands and those due to the phenyl rings listed by Doak, *et al.*,[20] two peaks at 795 (m, broad) and 528 cm^{-1} (m) were obtained for $(C_6H_5)_4SbOH$, examined in a KBr disk from 400 to 1200 cm^{-1}. The second of these bands lies close to the position of the Sb–O stretching mode[21] for $[SbF_5OH]^-$, while the band at 795 cm^{-1} is perhaps due to the Sb–O–H bending mode. In the spectrum of bis(tetraphenylantimony) oxide, the peaks at 3620 and 3320 cm^{-1} are absent while those at 795 and 528 cm^{-1} are replaced by a strong doublet at 652 and 660 cm^{-1}. Bands in the range 672–736 cm^{-1} for $[(C_6H_5)_3Sb\text{–}O\text{–}Sb(C_6H_5)_3]Y_2$ (where Y is a common inorganic anion) have been assigned to the Sb–O–Sb asymmetric stretching mode.[20]

(20) G. O. Doak, G. G. Long, and L. D. Freedman, *J. Organometal. Chem.*, **4**, 82 (1965).

(21) L. Kolditz and B. Nussbücker, *Z. Anorg. Allgem. Chem.*, **337**, 191 (1965).

The Stereochemistry of the Hexaoxo-μ-ethylenediaminetetraacetato-dimolybdate(VI) Ion in the Crystalline Sodium Salt and in Aqueous Solution[1,2]

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Abstract: A quantitative stereochemical description of the binuclear anion consisting of two molybdenum trioxide moieties that are bridged and stabilized through a complexing ethylenediaminetetraacetate ion (A^{4-}) emerges from the determination by X-ray analysis of the atomic arrangement in the crystalline sodium salt, $Na_4(O_3MoAMoO_3)\cdot 8H_2O$. The MoO_3 moiety in the octahedral coordination group of each Mo(VI) atom exhibits full double bonding with angles approaching the regular tetrahedral values, whereas the complexing links to nitrogen and carboxylate oxygen atoms carry, at most, bond orders of unity. The $O_3MoAMoO_3{}^{4-}$ complex, required in the crystal to possess a center of inversion, departs rather little from the higher symmetry of C_{2h}-2/m. The unit cell of the monoclinic crystals containing $2Na_4(O_3MoAMoO_3)\cdot 8H_2O$ has a = 8.50, b = 11.56, c = 13.36 Å, and β = 87.25; calculated and measured densities are 2.057 and 2.05 g/cc, respectively. The space group is $P2_1/c$. Some 3857 independent nonvanishing reflections, approximately 1.3 times the number comprised within the Cu Kα limiting sphere, were photographically recorded with Mo Kα radiation; intensities were visually estimated. Structure determination utilized Patterson and Fourier methods followed by anisotropic full-matrix least-squares refinement; a conventional R of 0.090 was obtained.

Pecsok and Sawyer[4] have presented polarographic evidence for the existence in aqueous solution of a binuclear anionic complex in which two molybdenum(VI) atoms presumably are bridged through an ethylenediaminetetraacetate ion (A^{4-}). Following crystallization and chemical analysis of the sodium salt, $Na_4(O_3MoAMoO_3)\cdot 8H_2O$, they proposed a pattern for the connexity of the atoms within the complex that puts the Mo(VI) atoms into octahedral coordination. A subsequent proton magnetic resonance (pmr) study by Chan, *et al.*,[5] suggests that in aqueous solution, pH 3–8, the chelate exists predominantly in a single stereoisomeric form that gives just one sharp resonance for the four protons of the central ethylene radical and one resonance quartet of AB type for the eight methylenic protons adjacent to carboxylate groups. When considered in conjunction with the postulated connexity of the atoms, the pmr data are consistent with any of several stereoisomeric forms of the $O_3MoAMoO_3{}^{4-}$ ion having the effective symmetry of either C_{2v} or C_{2h}.

The *a priori* identification of a single C_{2h} stereoisomer and of a single C_{2v} stereoisomer that can have octahedrally coordinated Mo(VI) atoms while fully observing the stringent stereochemical constraints that

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(2) The abbreviation, EDTA, and the short formula, AH_4, are used throughout for ethylenediaminetetraacetic acid.

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(4) R. L. Pecsok and D. T. Sawyer, *J. Am. Chem. Soc.*, **78**, 5696 (1956).

(5) S. I. Chan, R. J. Kula, and D. T. Sawyer, *ibid.*, **86**, 377 (1964).