nificant exchange broadening does not occur in the $^{13}C$ resonance of a typical mixture containing excess $(Me_2N)_3SiCl$ even at −90 °C. Thus, if the structure of $(Me_2N)_3SiCl{\cdot}AlCl_3$ in solution is the same as that in the solid state, the $AlCl_3$ moiety must be averaging among all three nitrogen sites fairly rapidly. The foregoing conclusions are consistent with the $^{27}Al$ NMR data for a 1:1 mixture of $(Me_2N)_3SiCl$ and $AlCl_3$ units (Figure 2b), since the $^{27}Al$ chemical shift of $(Me_2N)_3SiCl{\cdot}AlCl_3$ (+107 ppm) is close to that of other $R_3E{\cdot}AlCl_3$ complexes, such as $Me_3P{\cdot}AlCl_3$.[22] The $^{29}Si$ NMR data were difficult to obtain, possibly owing to quadrupolar relaxation effects associated with the $^{14}N$ nuclei. However, on cooling the samples (equimolar in $(Me_2N)_3SiCl$ and $AlCl_3$ units) to −60 °C it was possible to detect singlet resonances. The chemical-shift difference between $(Me_2N)_3SiCl$ and that which we attribute to $(Me_2N)_3SiCl{\cdot}AlCl_3$ is surprisingly small.

The interaction of $(Me_2N)_3SiF$ with the fluoride ion acceptors $PF_5$ and $AsF_5$ was explored as a potential synthetic route to the $[(Me_2N)_3Si]^+$ ion. These reactions are apparently complex, resulting in the appearance of several new resonances. However, none of these resonances was attributable to $PF_6^-$ or $AsF_6^-$; hence, this line of experimentation was not pursued further.

Current efforts to synthesize silicenium ions involve the use of cyclic precursor halides and silyl halides with both bulky and $\pi$-donor substituents.

**Acknowledgment.** The authors are grateful to the National Science Foundation (Grant CHE76-10331) and the Robert A. Welch Foundation for generous financial support. We also wish to thank the National Science Foundation for the purchase of the Syntex $P2_1$ diffractometer, and Professor Raymond E. Davis for his interest and assistance in this work.

**Supplementary Material Available:** A tabulation of observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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# Synthesis and Crystal Structure of Bis(triphenylantimony catecholate) Hydrate. A New Square-Pyramidal Antimony(V) Compound

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*Received July 12, 1979*

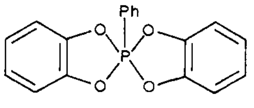
**Abstract:** Reaction between triphenylantimony dichloride and catechol in the presence of ammonia yields the partially hydrated product $(Ph_3SbO_2C_6H_4)_2{\cdot}H_2O$, the crystal structure of which has been determined by single-crystal X-ray diffraction methods. The compound, bis(2,2,2-triphenyl-1,3,2-benzodioxastibole) hydrate, crystallized in the monoclinic space group $P2_1/c$ with cell constants $a$ = 9.78 (1) Å, $b$ = 21.10 (1) Å, $c$ = 19.95 (1) Å, $\beta$ = 105.28 (5)°, $Z$ = 4. Antimony atoms in both five- and sixfold coordination are present with the central atom in the former being attached to three carbon and two oxygen atoms in a distorted square-pyramidal arrangement. Distortion of this polyhedron arises basically from the presence of the dioxo chelating group. The second polyhedron is distorted octahedral and is derived from the square-pyramidal arrangement above with the addition of a water molecule weakly coordinated in the sixth position.

Trigonal bipyramidal or square pyramidal based structures are generally considered possible for compounds in which the central atom has ten electrons in its valence shell. The difference in energy between these two forms is apparently small but, while both arrangements are found when the central atom is a transition element, compounds derived from main-group elements have with very few exceptions the trigonal-bipyramidal configuration. The major exception is the square-pyramidal structure found for pentaphenylantimony[1] where crystal-packing effects are thought to stabilize this geometry at the expense of the "expected" trigonal-bipyramidal form.[2] It is worth stressing the unusual situation with $SbPh_5$, as the $p$-tolyl antimony derivative[3] and pentaphenyl derivatives of arsenic and phosphorus[5] all have trigonal-bipyramidal

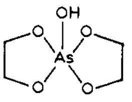
0002-7863/80/1502-0628$01.00/0

structures in the solid state. In addition, the cyclohexane adducts of both $Ph_5As$[6] and $Ph_5Sb$[7] each have trigonal-bipyramidal structures. Spectroscopic evidence has been interpreted as indicating square-pyramidal geometry for penta(cyclopropyl)antimony,[8] but crystallographic confirmation is lacking.

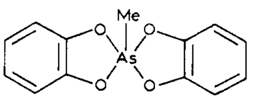
The general problem of the stereochemistry of five-coordinate compound of the group 5 elements has been extensively investigated over recent years. A major effort has been associated with phosphorus compounds and, in particular, Holmes and his co-workers[9] have prepared and identified a number of species in which there is a progressive distortion from trigonal-bipyramidal geometry along the Berry coordinate toward the square pyramid. Recently two five-coordinate arsenic compounds have been shown by X-ray crystallography to have structures which are similarly distorted from trigonal-bipyramidal geometry.[10,11] A common feature of these distorted structures for both phosphorus and arsenic is the presence of a dioxo chelating group as shown in I, II, and III. In these circumstances, it is a little surprising that for the analogous antimony compound (IV) the observed structure is very close to an ideal trigonal bipyramid.[12]



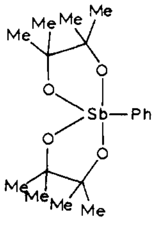
(I)



(II)



(III)



(IV)

We have recently investigated the reaction between catechol and triphenylantimony dichloride in the presence of ammonia, and it seemed appropriate to determine the structure of the product. When the product was first isolated, the analytical data appeared to support its formulation as $Ph_3Sb(O_2C_6H_4)$, but as a result of the structure determination the compound is to be formulated as the hemihydrate $2Ph_3Sb(O_2C_6H_4)\cdot H_2O$. A compound with the formula $Ph_3Sb(O_2C_6H_4)$ has been reported previously as the product from a reaction between triphenylantimony dibromide and the disodium salt of catechol.[13]

## Experimental Section

**Triphenylantimony Catecholate Hemihydrate.** Triphenylantimony dichloride and 1,2-dihydroxybenzene in a 1:1 molar ratio were dissolved in dry dichloromethane and dry gaseous ammonia was passed through the solution until no further precipitate formed. After the ammonium chloride was filtered off, the solution was concentrated and cooled to −5 °C, whereupon white crystals were obtained. The overall yield of pure material is low owing to its ready redox decomposition in solution, mp 149–151 °C. Anal. Calcd for $C_{24}H_{19}O_2Sb$: C, 62.5; H, 4.1. Calcd for $C_{48}H_{40}O_5Sb_2$: C, 61.3; H, 4.3. Found: C, 62.2; H, 4.0. The infrared spectrum showed absorptions characteristic of both types of attached groups but it was not possible to make structurally significant observations because of the general complexity. Thick, concentrated Nujol mulls, however, showed weak bands at 3476 and 3463 $cm^{-1}$, characteristic of coordinated water molecules. The highest *m/e* ion in the 70-eV mass spectrum could be assigned to the $Ph_3SbO_2C_6H_4^+$ ion (1.7% of the total ion current); other major ions identified were $Ph_3Sb^+$ (2.5%), $Ph_2Sb^+$ and related ions (3.0%), and $PhSb^+$ (23.0%). Traces only of ions such as $Ph_2SbO_2C_6H_4^+$, $PhSbO_2C_6H_4^+$, and $SbO_2C_6H_4^+$ were observed.

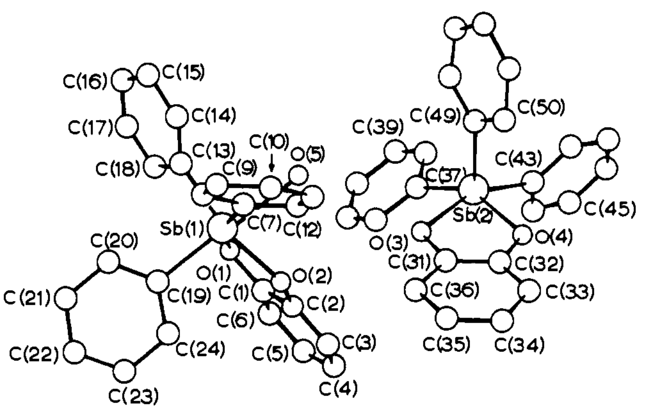


Figure 1. Structure of $(Ph_3SbO_2C_6H_4)_2\cdot H_2O$, showing the atom numbering scheme.

Crystals suitable for X-ray investigation were obtained by slow recrystallization at room temperature from dichloromethane and one with dimensions 0.3 × 0.2 × 0.5 mm was mounted on a glass fiber.

**Crystal Data.** $C_{48}H_{40}O_5Sb_2$, $M = 940$, monoclinic, $a = 9.78$ (1) Å, $b = 21.10$ (1) Å, $c = 19.95$ (1) Å, $\beta = 105.28$ (5)°, $V = 3970.5$ Å$^3$, $d_{calcd} = 1.59$ g cm$^{-3}$, $Z = 4$, $F(000) = 1880$, space group $P2_1/c$ from systematic absences, MoK$\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu$(Mo K$\alpha$) = 14.3 cm$^{-1}$.

**Structure Solution and Refinement.** The unit cell dimensions, initially obtained from oscillation and Weissenberg photographs, were refined by a least-squares procedure on the positions of 23 strong reflections accurately measured on a Hilger and Watts four-circle diffractometer. Intensity data were then collected using an $\omega$–$2\theta$ scan for 5984 reflections in the range $0° \leqslant \theta \leqslant 27°$, using Mo K$\alpha$ radiation. The intensities of the 5956 reflections for which $I > 3\sigma(I)$ were corrected for Lorentz and polarization effects but not for absorption or secondary extinction. Data reduction and subsequent crystallographic calculations used the CRYSTALS programs;[14] atom scattering factors were taken from ref 15.

The asymmetric unit contains two independent antimony atoms and a three-dimensional Patterson synthesis readily gave their probable positions. A difference Fourier synthesis phased on these refined positions showed, in addition to the expected six phenyl groups and two catechol residues, an extra peak in the vicinity of Sb(1) which was identified as an oxygen atom. This is presumably to be associated with a water molecule and Sb(1) is a monohydrate.

Six cycles of full-matrix, least-squares refinement gave convergence with isotropic thermal parameters at $R$ (conventional) = 6.67%, and with anisotropic thermal parameters $R$ converged at 3.94% after a further four cycles of full-matrix refinement. A difference Fourier synthesis at this stage showed a number of peaks associated with the hydrogen atoms of the phenyl groups but, as there was not a complete set, all these hydrogen positions were calculated. A further three cycles of refinement with fixed hydrogen positions gave convergence at $R$ = 3.06%. Analysis of the reflection data showed that unit weights were appropriate. It was not possible from a final difference Fourier synthesis to locate the hydrogen atoms attached to O(5), the hydrate water molecule, but the difference map showed clearly that hydration had occurred at Sb(1) only. The only peaks with an intensity greater than 0.4 e Å$^{-3}$ were associated with residual anisotropy about the antimony atoms. Refined values for the fractional atomic coordinates and the anisotropic thermal parameters are listed in Tables I and II,[21] respectively. Calculated hydrogen atom positions for the phenyl groups are collected in Table III.[21]

## Results and Discussion

Table IV summarizes the important bond distances and angles in the two molecules, while other dimensions associated with the phenyl and catechol groups are collected in Table V.[21] A diagram showing the two molecules and including the atom numbering scheme is given in Figure 1.

The structure determination shows that the hydrated catecholate contains antimony atoms in both six- and fivefold

**Table I.** Final Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses

| atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Sb(1) | 2863.9(3) | 3849.6(1) | 3276.8(1) |
| O(1) | 2990(3) | 4420(1) | 4122(1) |
| O(2) | 3740(3) | 3230(1) | 4063(1) |
| O(5) | 691(4) | 3484(2) | 3613(2) |
| C(1) | 3677(4) | 4138(2) | 4731(2) |
| O(2) | 4039(4) | 3499(2) | 4701(2) |
| C(3) | 4672(4) | 3174(2) | 5301(2) |
| C(4) | 4997(5) | 3496(2) | 5936(2) |
| C(5) | 4679(5) | 4131(2) | 5962(2) |
| C(6) | 4015(4) | 4457(2) | 5359(2) |
| C(7) | 2504(4) | 3022(2) | 2631(2) |
| C(8) | 2790(5) | 3045(2) | 1985(2) |
| C(9) | 2764(5) | 2495(3) | 1600(2) |
| C(10) | 2448(5) | 1925(2) | 1857(3) |
| C(11) | 2130(5) | 1899(2) | 2489(3) |
| C(12) | 2143(5) | 2449(2) | 2872(2) |
| C(13) | 1436(4) | 4519(2) | 2656(2) |
| C(14) | 1508(5) | 5153(2) | 2849(2) |
| C(15) | 617(6) | 5591(2) | 2436(3) |
| C(16) | −323(6) | 5404(3) | 1825(3) |
| C(17) | −394(6) | 4778(3) | 1633(3) |
| C(18) | 479(5) | 4335(2) | 2047(2) |
| C(19) | 4823(5) | 4188(2) | 3126(2) |
| C(20) | 4852(5) | 4541(2) | 2540(3) |
| C(21) | 6135(7) | 4784(3) | 2474(3) |
| C(22) | 7372(6) | 4680(3) | 2985(3) |
| C(23) | 7337(5) | 4329(3) | 3562(3) |
| C(24) | 6072(5) | 4080(2) | 3630(2) |
| Sb(2) | −599.9(3) | 2154.7(1) | 5169.4(1) |
| O(3) | 1162(3) | 2235(1) | 4793(2) |
| O(4) | 373(3) | 1326(1) | 5490(2) |
| C(31) | 1912(4) | 1687(2) | 4847(2) |
| C(32) | 1488(5) | 1202(2) | 5217(2) |
| C(33) | 2169(6) | 622(3) | 5302(3) |
| C(34) | 3287(6) | 533(3) | 5005(4) |
| C(35) | 3715(5) | 1011(3) | 4644(3) |
| C(36) | 3047(5) | 1599(2) | 4565(3) |
| C(37) | −564(4) | 3158(2) | 5261(2) |
| C(38) | −1796(4) | 3422(2) | 5358(2) |
| C(39) | −1866(5) | 4068(2) | 5482(2) |
| C(40) | −691(5) | 4443(2) | 5528(2) |
| C(41) | 542(5) | 4181(2) | 5433(2) |
| C(42) | 614(4) | 3540(2) | 5290(2) |
| C(43) | −1690(5) | 2000(2) | 5957(2) |
| C(44) | −1276(5) | 2323(2) | 6584(2) |
| C(45) | −2022(6) | 2237(3) | 7083(3) |
| C(46) | −3169(7) | 1837(3) | 6950(3) |
| C(47) | −3592(6) | 1519(3) | 6325(3) |
| C(48) | −2847(6) | 1601(3) | 5825(3) |
| C(49) | −2091(4) | 1869(2) | 4257(2) |
| C(50) | −3108(6) | 2267(3) | 3889(3) |
| C(51) | −4120(6) | 2056(3) | 3310(3) |
| C(52) | −4102(6) | 1442(3) | 3096(3) |
| C(53) | −3075(7) | 1041(3) | 3465(4) |
| C(54) | −2074(6) | 1246(3) | 4047(3) |

coordination. The geometry about Sb(1) is best described as distorted octahedral with bonds to three phenyl groups and three oxygen atoms; as perhaps expected, the groups of carbon and oxygen atoms each occupy a triangular face giving the *fac*-isomeric form. Bonds between Sb(1) and the three phenyl groups are identical and of normal length, as are those with the oxygen atoms of the catechol group. The distance between Sb(1) and O(5), the oxygen atom of the hydrate water molecule, is exceedingly long (2.512 Å) and must imply very weak interaction with the central antimony atom. Most available data on Sb(V)-oxygen bond distances refer to $SbCl_5$ addition compounds with values from 1.94 (for $SbCl_5 \cdot Me_3PO$)[16] to 2.42 Å ($2SbCl_5$·succinyl chloride)[17] being reported. In the monohydrate of diphenylantimony trichloride the analogous distance is 2.21 Å.[18] The present compound must therefore represent one of the weakest known donor bonds to antimony(V); a bond order of 0.17 can be assigned using Pauling's equation.[19]

Bond distances to Sb(2), which is in distorted square-pyramidal coordination (see below), are similar to those already discussed but distances to the catechol oxygens and the carbon atoms are not equivalent and are indicative of a small degree of residual trigonal-bipyramidal character. The distance to C(49), which occupies the apical position in the square pyramid, is significantly shorter than any other and, as such, falls into the expected pattern of distances for this coordination polyhedron. The bond shortening is, however, much less than that observed for $Ph_5Sb$.[1]

The distorted octahedral geometry about Sb(1) can be illustrated by the three planes described by the ligands (see Table VI). These are roughly orthogonal but in each case the antimony atom is displaced from the appropriate best plane in the direction of the phenyl group not included in that plane. The maximum deviation is 0.29 Å from the O(1)-O(2)-C(7)-C(13) plane toward C(19). These distortions can be considered in more detail by examining the bond angles at Sb(1). For convenience let C(19) and O(5) be designated as "axial" atoms in the distorted octahedron about Sb(1). The equatorial plane is then 0.29 Å from the antimony atom in the direction of O(5), as expected since the O(5) water molecule is participating in weak donor-acceptor interaction only. Confirming this distortion is the fact that the four equatorial angles sum to 355.5° only (mean 88.9°). Further, the trans equatorial angles are ca. 160°.

Constraints in the five-membered ring system reduce the O(1)-Sb(1)-O(2) angle to 79.8°, a value commonly found in such chelate systems, while the C(7)-Sb(1)-C(13) angle opposite in compensation is increased to 102.3°. Mean values for the axial-equatorial angles for C(19) and O(5) are 97.8 and 81.8°, again showing that the antimony atom is considerably above the equatorial plane.

There is a strong similarity between the geometry at Sb(2) and that at Sb(1), with the obvious exception that there is no water molecule attached in the sixth position at Sb(2), and to discuss the structure in terms of anything other than a distorted square pyramid would be an error. In confirmation of this statement is an average deviation per X-Sb-Y angle of 4.4° assuming square-pyramidal geometry but 12.6° for trigonal-bipyramidal geometry assuming that O(4) and C(43) occupy the axial positions. We have mentioned earlier that the apical bond distance, Sb(2)-C(49), is short compared with the two basal Sb-C bonds as required in square-pyramidal geometry. Removal of the hydrate water molecule in this second antimony molecule has the effect of lifting the antimony atom still further (0.50 Å) above the basal plane [O(3)-O(4)-C(37)-C(43)], and allowing greater geometrical freedom for these four atoms. These now show a mean deviation of 0.08 Å from the best plane compared with 0.02 Å for the atoms in the analogous plane for the Sb(1) molecule.

The mean value for the angles between C(49) and the four basal atoms is 103.5° (cf. 105° for an ideal square pyramid), though the individual angles vary between 99.5 and 110.7°. The major factor responsible for this spread is of course the presence of the chelating catechol group. Cis basal angles in a square pyramid have an ideal value of 86° but that involving the catechol group, O(3)-Sb(1)-O(4), is of a necessity reduced to 79.4°. In compensation, as found in the Sb(1) molecule, the opposite angle is opened, in this case to 95.1°. The trans basal angles of 154.9 and 147.4° are close to the ideal value of 150°.

The carbon ring systems in both molecules are planar with C-C bond lengths of 1.38 ± 0.02 Å, and with two exceptions the angles at each carbon are close to 120°. Both these devia-

**Table IV.** Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

| | |
|---|---|
| Sb(1)-O(1) | 2.049(3) |
| Sb(1)-O(2) | 2.048(3) |
| Sb(1)-O(5) | 2.512(4) |
| Sb(1)-C(7) | 2.143(4) |
| Sb(1)-C(13) | 2.138(4) |
| Sb(1)-C(19) | 2.139(4) |
| O(1)-C(1) | 1.360(5) |
| O(2)-C(2) | 1.352(5) |
| C(19)-Sb(1)-O(1) | 93.3(1) |
| C(19)-Sb(1)-O(2) | 96.4(1) |
| C(19)-Sb(1)-C(7) | 101.5(2) |
| C(19)-Sb(1)-C(13) | 99.9(2) |
| C(19)-Sb(1)-O(5) | 172.8(2) |
| O(1)-Sb(1)-O(2) | 79.8(1) |
| O(1)-Sb(1)-C(7) | 159.7(1) |
| O(1)-Sb(1)-C(13) | 88.6(1) |
| O(1)-Sb(1)-O(5) | 80.4(1) |
| O(2)-Sb(1)-C(7) | 84.8(1) |
| O(2)-Sb(1)-C(13) | 160.6(1) |
| O(2)-Sb(1)-O(5) | 79.2(1) |
| C(7)-Sb(1)-C(13) | 102.3(2) |
| C(7)-Sb(1)-O(5) | 83.9(2) |
| C(13)-Sb(1)-O(5) | 83.6(2) |
| Sb(1)-C(7)-C(8) | 119.2(3) |
| Sb(1)-C(7)-C(12) | 121.4(3) |
| Sb(1)-C(13)-C(14) | 119.9(3) |
| Sb(1)-C(13)-C(18) | 120.8(3) |
| Sb(1)-C(19)-C(20) | 120.9(3) |
| Sb(1)-C(19)-C(24) | 119.8(3) |
| Sb(1)-O(1)-C(1) | 112.7(2) |
| Sb(1)-O(2)-C(2) | 113.3(2) |
| O(1)-C(1)-C(2) | 117.0(4) |
| O(2)-C(2)-C(1) | 116.8(4) |
| O(1)-C(1)-C(6) | 122.7(4) |
| O(2)-C(2)-C(3) | 123.0(4) |
| Sb(2)-O(3) | 2.060(3) |
| Sb(2)-O(4) | 2.013(3) |
| Sb(2)-C(37) | 2.125(4) |
| Sb(2)-C(43) | 2.143(4) |
| Sb(2)-C(49) | 2.099(4) |
| O(3)-C(31) | 1.359(5) |
| O(4)-C(32) | 1.366(5) |
| C(49)-Sb(2)-O(3) | 99.5(2) |
| C(49)-Sb(2)-O(4) | 100.9(2) |
| C(49)-Sb(2)-C(37) | 110.7(2) |
| C(49)-Sb(2)-C(43) | 103.0(2) |
| O(3)-Sb(2)-O(4) | 79.4(1) |
| O(3)-Sb(2)-C(37) | 87.3(1) |
| O(3)-Sb(2)-C(43) | 154.9(1) |
| O(4)-Sb(2)-C(37) | 147.4(2) |
| O(4)-Sb(2)-C(43) | 85.4(2) |
| C(37)-Sb(2)-C(43) | 95.1(2) |
| Sb(2)-C(37)-C(38) | 114.7(3) |
| Sb(2)-C(37)-C(42) | 125.0(3) |
| Sb(2)-C(43)-C(44) | 120.2(3) |
| Sb(2)-C(43)-C(48) | 119.7(4) |
| Sb(2)-C(49)-C(50) | 122.2(4) |
| Sb(2)-C(49)-C(54) | 118.4(4) |
| Sb(2)-O(3)-C(31) | 112.7(3) |
| Sb(2)-O(4)-C(32) | 113.5(3) |
| O(3)-C(31)-C(32) | 116.1(4) |
| O(4)-C(32)-C(31) | 116.9(4) |
| O(3)-C(31)-C(36) | 123.7(4) |
| O(4)-C(32)-C(33) | 121.9(5) |

**Table VI.** Selected Molecular Planes

| atoms in plane | deviations from mean plane, Å | | | | | |
|---|---|---|---|---|---|---|
| O(1) O(2) C(7) C(13) | O(1) | 0.017, | O(2) | −0.017, | C(7) | 0.014, |
| | C(13) | −0.013, | Sb(1) | 0.294, | C(19) | 2.425 |
| O(1) O(5) C(7) C(19) | O(1) | −0.084, | O(5) | 0.081, | C(7) | −0.072, |
| | C(19) | 0.075, | Sb(1) | 0.162, | C(13) | 2.262 |
| O(2) O(5) C(13) C(19) | O(2) | −0.029, | O(5) | 0.029, | C(13) | −0.025, |
| | C(19) | 0.026, | Sb(1) | 0.149, | C(7) | 2.242 |
| O(3) O(4) C(37) C(43) | O(3) | 0.075, | O(4) | −0.077, | C(37) | −0.061, |
| | C(43) | 0.063, | Sb(2) | 0.497, | C(49) | 2.584 |

tions are associated with C(37) [Sb(2)-C(37)-C(38), 114.7°; Sb(2)-C(37)-C(42), 125.0°]. The only close contact involving C(37) is with O(5) at 3.86 Å and it is difficult to see any relationship with the distortion.

There are two important points arising from this structure determination. The first concerns the interaction between one of the catecholate molecules and an adventitious water molecule. Although this is clearly very weak, it is nevertheless a surprising observation as the Lewis-acid character of $Ph_3SbX_2$ compounds is apparently very low. Whereas a number of $Ph_2SbX_3$ and $PhSbX_4$ compounds readily accept a pair of electrons from a halide ion or other Lewis base, similar compounds cannot be isolated from the triphenylantimony(V) analogues. In $Ph_3Sb(O_2CCH_3)_2$, however, there seems to be residual Lewis acidity associated with the antimony atoms as weak intramolecular bonds (Sb· · ·O, 2.78 Å) are formed with the nonbonded oxygen atoms of the acetate groups.[20]

The second point concerns the square-pyramidal geometry about the five-coordinate antimony atom. It is difficult in this case to ascribe to crystal-packing effects alone this stabilization of the less usual square-pyramidal geometry. Such an explanation may be necessary in the case of pentaphenylantimony but here it is likely that geometrical constraints imposed on the system by the presence of the catechol residue are more important. However, it is clear that the mere incorporation of a chelating dioxo ligand does not lead to square-pyramidal geometry. For example, the spirocyclic $PhSb(O_2C_2Me_4)_2$ (IV), in which the chelating groups have the same "bite" (2.6 Å) as found in the present catecholate, has a trigonal-bipyramidal structure.

It is hoped that some clarifaction of both these points will be forthcoming when the detailed structure of the anhydrous catecholate is known. Experiments in this direction are in progress.

**Supplementary Material Available:** Anisotropic thermal parameters (Table II), calculated hydrogen atom positions (Table III), bond distances and angles associated with the phenyl groups (Table V), and a listing of structure factors for $(Ph_3SbO_2C_6H_4)_2 \cdot H_2O$ (17 pages). Ordering information is given on any current masthead page.

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# Model Networks of End-Linked Polydimethylsiloxane Chains. 5. Dependence of the Elastomeric Properties on the Functionality of the Network Junctions

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*Received June 18, 1979*

**Abstract:** Elastomeric networks of carefully controlled structure were prepared by end-linking hydroxyl-terminated polydimethylsiloxane chains of known molecular weight by means of a trialkoxysilane $(C_2H_5O)_3RSi$. The reactions were carried out both in the undiluted state and in solution, in order to assure stoichiometric completeness in the formation of the network structures. The trifunctional networks thus prepared were studied with regard to their stress–strain isotherms in the unswollen state, in elongation at 25 °C, and with regard to their equilibrium swelling in benzene at room temperature. Values of the modulus in the limits of large and small deformations were found to be in satisfactory agreement with theoretical predictions for nonaffine and affine deformations, respectively (the latter corresponding to the case in which the displacements of the network chain vectors are a simple linear function of the macroscopic strain). Comparisons with results previously obtained on the corresponding tetrafunctional networks showed that both of these moduli have very nearly the expected dependence on network functionality. The equilibrium swelling data were interpreted to estimate the extent to which the swelling deformation approaches the affine limit. The results for both the trifunctional and tetrafunctional networks are in very good agreement with a recent theory of network swelling in which the closeness of the approach to the affine limit depends on both the network structure and the degree of swelling.

## Introduction

One of the most striking properties of flexible polymer chains is the rubberlike elasticity they exhibit when cross-linked into network structures.[1,2] Although this unique type of elastic behavior has been under investigation for over a century now, there are still a number of important unresolved issues in this area. The most important of these concerns the relationships between the equilibrium elastomeric properties of a polymer network and the details of its molecular structure. Relatively little has been accomplished in definitively establishing such relationships because of serious difficulties in obtaining independent information on the network structure. The method of preparation of the network seldom provides information in this regard because of the highly random, uncontrolled manner in which the cross-links are usually introduced.[1,2]

It is now possible, however, to prepare "model" networks in which important characteristics of the network structure are known and controllable, because of the selectivity of the cross-linking reaction. One of the most useful chemical reactions of this type involves linking the chains exclusively through functional groups placed at their two ends.[3-9] The crucially important molecular weight $M_c$ between cross-links is then simply the (known) molecular weight of the chains prior to their incorporation into the network structure. Furthermore, with this technique it is also possible to vary the functionality $\phi$ of a network cross-link (the number of chains emanating from it) by suitable choice of end-linking reactant.

The present study involves the preparation of end-linked polydimethylsiloxane (PDMS) networks having known network chain length, and a known cross-link functionality of three, instead of the usual functionality of four. The networks are characterized with regard to their stress–strain isotherms in elongation and their degree of equilibrium swelling in a thermodynamically good solvent. The results are used to establish the relationship between the modulus of a network and its degree of cross-linking or, equivalently, the molecular weight $M_c$ of its network chains. The equilibrium swelling data are employed primarily to estimate the extent to which the swelling deformation approaches the affine limit, in which the molecular dimensions are assumed to vary linearly with the changes in the macroscopic dimensions of the elastomeric sample. Comparisons with previously published results on the corresponding tetrafunctional PDMS networks are then used to elucidate the effect of cross-link functionality on the elastomeric properties of polymer networks.

## Experimental Section

The polymer used was an unfractionated sample[3,5,7,8,10] of PDMS having hydroxyl groups at both ends, a number-average molecular

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