Synthesis and Laser-Raman and Infrared Spectra of Pentacyclopropylantimony(V)—A New Square-Pyramidal Molecule

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Abstract: The syntheses of the new compounds tricyclopropylstibine and pentacyclopropylantimony(V) are reported. The infrared and laser-Raman spectra of the yellowish liquid $(c\text{-}C_3H_5)_5Sb$ are measured and the fundamentals are assigned by comparison to the vibrational spectrum of bromocyclopropane, whose Raman spectrum is redetermined. The vibrational display for the pentacoordinate antimony species in the low-frequency region (600–200 cm^{-1}) is consistent with a square-pyramidal molecular framework and does not agree with that anticipated for a trigonal-bipyramidal geometry.

Whereas it is not possible to isolate cyclopropyl derivatives of the transition metals,[2] the nontransition elements appear to form cyclopropyl-substituted compounds quite readily. At the present time the literature contains reports of cyclopropyl compounds of lithium,[3] boron,[4] magnesium,[5] aluminum,[6] silicon,[7] phosphorus,[8] gallium,[7b] germanium,[7] indium,[7b] tin,[7a] and mercury.[9] Much of the recent work has been stimulated by the possibility that the cyclopropyl moiety might exert unusual effects on the bonding and stereochemistry of organometallic compounds. A case in point is the enhanced stability of the hydrocarbon bridge in the tricyclopropylaluminum dimer.[6] More generally, it is known that the cyclopropyl group can function as both a π-electron acceptor and a π-electron donor.

The former behavior is, in fact, a well-known effect in organic chemistry,[10] while the latter has been noted in certain cyclopropyl-substituted anion radicals.[11] In turn these conjugative considerations pose an interesting question in regard to the possible effects of the cyclopropyl substituent on the stereochemistry of pentacoordinate species. In particular, we were interested in the synthesis and structure determination of pentacyclopropylantimony to ascertain whether, like its phenyl analog $(C_6H_5)_5Sb$,[12] it adopts a square-pyramidal skeletal geometry. Interestingly, at the inception of this study, $(C_6H_5)_5Sb$ appeared to be the only nonionic pentacoordinate species in group V which does not possess a trigonal-bipyramidal framework, but a recent infrared study concludes that SbF_5 is also square pyramidal in rare gas matrices.[13] Indeed, even the majority of tetraphenylantimony(V) derivatives appear to be molecular, five coordinate, and trigonal bipyramidal.[14] It was also hoped that a knowledge of the structure of $(c\text{-}C_3H_5)_5Sb$ might provide some indirect evidence concerning the importance of crystal packing considerations in relation to the structure of $(C_6H_5)_5Sb$.

Experimental Section

Syntheses. General. The materials $c\text{-}C_3H_5Br$, $SbCl_3$, Li, and Br_2 were procured commercially and used without further purification. All solvents were dried and distilled prior to use.

All reactions and manipulations were performed under an atmosphere of dry nitrogen.

Tricyclopropylstibine. Cyclopropyllithium was prepared by the procedure of Seyferth and Cohen[3] from 5.5 g (0.800 mol) of lithium wire and 48.4 g (0.400 mol) of cyclopropyl bromide in 220 ml of anhydrous diethyl ether at 0°. A solution of 30.4 g (0.133 mol) of anhydrous $SbCl_3$ in 50 ml of dry $(C_2H_5)_2O$ was then added dropwise to the stirred cyclopropyllithium solution at 0°. The reaction was completed by gentle refluxing for 1.5 hr after completing the addition. The reaction mixture was then cooled to 0° and hydrolyzed by slow addition of 100 ml of a saturated NH_4Cl solution. After drying the ether layer over anhydrous Na_2SO_4 for 24 hr the solvent was stripped off *in vacuo* and the brown oily liquid residue was fractionally vacuum distilled. The major fraction (7.0 g, 28.5 mmol) boiled in the range 61–65° (1.1 mm), corresponding to a 21.4% yield. *Anal.* Calcd for $C_9H_{15}Sb$: C, 44.13; H, 6.17. Found: C, 46.55; H, 6.38. The 60-MHz ^1H nmr spectrum of $(c\text{-}C_3H_5)_3Sb$ (neat liquid) consisted of a complex multiplet centered at τ 8.3.

Pentacyclopropylantimony. Pentacyclopropylantimony was prepared by an analogous procedure to that described[15] for the synthesis of $(CH_3)_5Sb$. First a solution of $(c\text{-}C_3H_5)_3SbBr_2$ was prepared by slow addition of approximately 4.12 g (25.8 mmol) of Br_2 in 20 ml of CCl_4 to an equimolar quantity of $(c\text{-}C_3H_5)_3Sb$ dissolved in 50 ml of $(C_2H_5)_2O$. Addition of Br_2 was discontinued as soon as the bromine color persisted. A solution of 2.64 g (55.0 mmol) of $c\text{-}C_3H_5Li$ in 30 ml of $(C_2H_5)_2O$ was then added dropwise to the

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[1] (a) University of Texas; (b) Oregon Graduate Center; (c) Pennsylvania State University.

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Table I. Vibrational Spectra of $(c\text{-}C_3H_5)_5Sb$ and C_3H_5Br

C_3H_5Br[a]		$(c\text{-}C_3H_5)_5Sb$[b]		
Raman[c]	Infrared[d]	Raman	Infrared	Assignment
3089 (m, sh, dp)	3092 (m)	3056 (mw, dp)	3063 (m)	$\nu_{13} + \nu_{14}$ (A″, nonsym and sym CH_2 str)
3062 (m, p?)	3062 (w)			ν_2 (A′, nonsym CH_2 str)
3012 (s, p)	3012 (s)	2990 (vs, p)	2990 (s)	ν_1 (A′, sym CH_2 str)
2962 (vw, p)	2957 (w)			ν_3 (A′, CHBr str)
2920 (vw, p)				
2888 (vw, p)		2898 (vvw)		$2\nu_4$
			2870 (w)	$\nu_4 + \nu_{15}$
2835 (vw, p)		2850 (vvw)	2857 (vw, sh)	$2\nu_{15}$
1642 (w, p)				$\nu_{14} - \nu_4$
1446 (w, p?)	1446 (s)		1454 (s)	ν_4 (A′, sym CH_2 def)
1422 (mw, dp)	1422 (s)	1433 (w, dp?)	1431 (s)	ν_{15} (A″, asym CH_2 def)
1290 (vw, p)				$\nu_{10} + \nu_{11}$
1263 (w, dp)	1262 (vs)	1240 (w, dp)	1240 (ms)	ν_{16} (A″, asym CH_2 twist)
1232 (vvw)	1237 (w)		1235 (ms)	ν_5 (A′, sym CH_2 twist)
1200 (vs, p)	1199 (m)	1190 (vs, p)	1186 (s)	ν_6 (A′, sym ring contraction and expansion)
1165 (w, sh, dp)	1162 (w)		1167 (mw)	$\nu_9 + \nu_{21}$
1090 (vw, dp)	1092 (w)			$\nu_{12} + \nu_{20}$, $2\nu_{11}$
			1095 (mw)	
1050 (vw, dp)	1050 (s)		1050 (m)	ν_{17} (A″, asym CH_2 wag)
	1033 (sh)			ν_7 (A′, sym ring def) +
1026 (vw, p)	1023 (vs)	1028 (vw, p)	1025 (vs)	ν_8 (A′, sym CH_2 wag)
			995 (w, sh)	2(Sb–C str) (A_1)
927 (mw, dp)	926 (s)	857 (mw, dp)		ν_{18} (A″, asym ring def)
914 (vvw)				ν_{19} (A″, asym CH_2 rock)
863 (s, p)	863 (s)	875 (m, p)	871 (vs)	ν_9 (A′, sym CH_2 rock)
808 (w, dp)	805 (s)			ν_{20} (A″, asym CHBr def)
		e	812 (s)	Asym CHSb def (A″)
			785 (m)	Sym CHSb def (A′)
760 (mw, p)	759 (m)			ν_{10} (A′, sym CHBr def)
689 (w, dp)			*f*	
546 (vs, p)	547 (s)			ν_{11} (A′, C–Br str)
508 (vvw)				$\nu_{20} - \nu_{21}$
		503 (m, p)	503 (s)	Sb–C str (A_1)[g]
		475 (s, p)	477 (m, sh)	Sb–C str (A_1)
455 (vw, p)				
388 (vw, p)				
310 (mw, dp)	309 (vw)			ν_{21} (A″, asym C–Br def)
			310 (w)	Apical Sb–C def (E)
			300 (w)	Sb–C_4 in-plane def (E)
		294 (w, dp)		Sb–C_4 out-of-plane def (B_1)
273 (vs, p)	272 (m)			ν_{12} (A′, sym C–Br def)
		268 (w, dp)		Sb–C_4 in-plane def (B_2)
219 (vw, dp)				
		224 (s, p)		Sb–C_4 sym out-of-plane def (A_1)

[a] Neat liquid. [b] In CS_2 solution. Solvent bands omitted. [c] All frequencies in cm^{-1}. Abbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder; p, polarized; dp, depolarized. [d] From ref 16. Modal designations and approximate descriptions for C_3H_5Br are also taken from this reference. [e] Solvent bands at 810 and 801 cm^{-1} mask this region in the Raman spectrum. [f] A very broad, medium-intensity absorption is centered at 620 cm^{-1} in the infrared spectrum of neat $(c\text{-}C_3H_5)_5Sb$ which vanishes in the spectra of CS_2 solutions. The assignment of this mode is uncertain. [g] Graphical illustration of the normal modes of a square-pyramidal species is given in S. R. Leone, B. Swanson, and D. F. Shriver, *Inorg. Chem.*, 9, 2189 (1970). We thank Professor Shriver for providing a copy of this manuscript prior to publication.

stirred solution of $(c\text{-}C_3H_5)_3SbBr_2$ at 0°, resulting in the production of a copious white precipitate. After filtration of the reaction mixture and stripping off the solvent from the filtrate the crude product was fractionally vacuum distilled. A fraction boiling at 100° (0.15 mm) corresponded to a 10% yield of yellowish liquid $(c\text{-}C_3H_5)_5Sb$. *Anal.* Calcd for $C_{15}H_{25}Sb$: C, 55.08; H, 7.70. Found: C, 55.60; H, 6.37. The 60-MHz ^1H nmr spectrum (neat liquid) consisted of a complex multiplet centered at τ 8.7.

Spectral Measurements. The infrared spectra were measured in the region 4000–200 cm^{-1} on a carefully calibrated, air-dried Perkin-Elmer Model 621 grating infrared spectrometer. The material was sampled as a liquid film and in CS_2 solution on KRS-5 plates, and spectra of the CS_2 solutions were also measured in 0.1-mm polyethylene cells. Frequency accuracy is better than ±2 cm^{-1}.

The Raman spectra excited by a Spectra-Physics Model 125 He–Ne laser (output 68 mW) were measured with a Jarrell-Ash Model 25-300 laser-Raman spectrophotometer. Spectra were measured of the neat liquid in the sealed ampules into which it had been distilled and of CS_2 solutions of the material in a Perkin-Elmer multipass cell. Polarization properties were determined by accurately rotating the plane of polarization of the incident beam through 90°. The spectrophotometer was frequency calibrated using neon emission lines, and frequency placement is accurate to ±3 cm^{-1}, except for weaker broad bands. The spectrum of C_3H_5Br was also measured using the multipass cell.

Results

The laser-Raman spectrum of $(c\text{-}C_3H_5)_5Sb$ in CS_2 solution is shown in both polarization modes in Figure 1 and is tabulated in Table I. The infrared spectrum is also recorded in this table, along with the vibrational spectrum of liquid C_3H_5Br. The assignments for bromocyclopropane differ from those of Rothschild[16]

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(16) W. G. Rothschild, *J. Chem. Phys.*, 44, 1712, 3875 (1966).

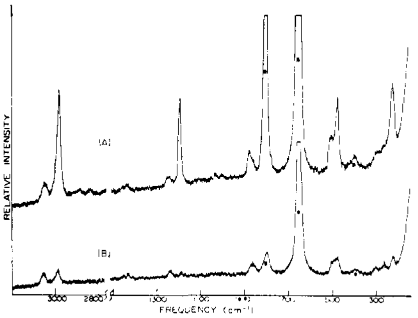

Figure 1. The laser-Raman spectrum of $(C_3H_5)_5Sb$: (A) $I_{\|}$, (B) $I_{\perp}$. CS_2 bands are starred.

only for fundamentals that were very weak and questionable in his Raman spectrum, but which are clearly measured in our laser-excited spectrum. Rothschild's modal descriptions and frequency numbering are adopted. The assignments of the $(c\text{-}C_3H_5)_5Sb$ modes above 600 cm^{-1} can be made empirically by comparison with the spectrum of cyclopropane and by observing the shifts and splittings of the modes of the parent compound on monosubstitution.[16] The spectrum of the antimony compound is juxtaposed to that of C_3H_5Br because the frequencies of cyclopropyl vibrations appear to be similar for these two molecules.

In the region below 600 cm^{-1} in the $(c\text{-}C_3H_5)_5Sb$ spectra, bands appear that are characterizable as antimony–ligand stretching and deformation modes, and these modes should reflect the skeletal geometry of the molecule. A fundamental that involves substantial cyclopropyl–substituent motion[16] may be viewed as coupling with the other four (identical) $Sb\text{–}C_3H_5$ modes of the pentacoordinate antimony compound to produce molecular modes. For example, the five cyclopropyl–antimony stretches (equivalent to ν_{11} for C_3H_5Br, the cyclopropyl–bromine stretch) couple to produce new stretching modes whose number and symmetry is determined by the framework geometry. To the extent that these modes do not interact with cyclopropyl ring modes, they may be described as those of a square-pyramidal or trigonal-bipyramidal MX_5 molecule. Thus, if pentacyclopropylantimony(V) is square pyramidal, one would expect nine Raman-active fundamentals below 600 cm^{-1} of symmetry $3A_1$, $2B_1$, B_2, and 3E,[17] and the A_1 and E modes are also infrared active. If the molecule is trigonal bipyramidal, six Raman-active ($2A_1'$, $3E'$, E'') and five infrared-active ($2A_2''$, $3E'$) modes would be expected in this region. Normal mode descriptions for both skeletal geometries have been provided previously.[18,19] For $(c\text{-}C_3H_5)_5Sb$, the low-frequency spectrum is in better agreement with that anticipated for C_{4v} skeletal symmetry (*vide infra*), and it is so assigned.

Discussion

The vibrational predictions for the polyhedra of C_{4v} and D_{3h} symmetry are summarized in Table II. A comparison of the low-frequency spectrum (below 600 cm^{-1}) of pentacyclopropylantimony(V) in Table I with the vibrational predictions in Table II shows that a square-pyramidal structure for this molecule is likely, although the spectra are apparently incomplete. Specifically, the evidence favoring this structure is the following. (a) Two relatively strong shifts appear in the Raman spectrum of the CS_2 solution at 503 and 475 cm^{-1}, and these polarized shifts are assigned as antimony–cyclopropyl stretching modes. Antimony–methyl stretches are measured at only slightly higher frequencies in the spectrum of $Sb(CH_3)_5$,[20] which appears to be trigonal bipyramidal, however. Infrared absorptions are measured at spectral positions (503 and 477 cm^{-1}) coincident with the Raman lines. Although two polarized Raman-active stretches are anticipated for either geometry, only for a C_{4v} skeleton would the polarized lines be coincident with infrared absorptions. For neat $(c\text{-}C_3H_5)_5Sb$ these bands are shifted to 492 and 472 cm^{-1}, respectively, in both the infrared and Raman spectra, and they are polarized. Other bands are slightly shifted. It therefore appears that the structure is identical in both CS_2 solution and in the neat liquid, and that environmental effects are not important. (b) A third strong polarized Raman line appears at 224 cm^{-1}. While three fully symmetrical fundamentals are allowed for a square-pyramidal geometry, only two polarized bands would be predicted for a trigonal-bipyramidal species. Unfortunately, this mode lies at the low-energy limit of our infrared spectrometer, and it is difficult to determine if a coincident frequency appears in absorption, although some spectra did show evidence of this. (c) This third polarized band appears in the region of deformational modes. For D_{3h} symmetry, polarized deformations are not predicted, but a single such fundamental is permitted under C_{4v} selection rules. If it is additionally acknowledged that doubly degenerate fundamentals are often weak in the Raman effect,[21] then our inability to identify Raman shifts above noise coincident with the infrared absorptions in the range 350–300 cm^{-1} may be rationalized.

Table II. Comparison of Predictions for Antimony–Cyclopropyl Skeletal Modes for Trigonal-Bipyramidal and Square-Pyramidal Geometries

	Trigonal bipyramid (D_{3h})	Square pyramid (C_{4v})
Raman-active modes	6 ($2A_1'$, $3E'$, E'')	9 ($3A_1$, $2B_1$, B_2, 3E)
Infrared-active modes	5 ($2A_2''$, $3E'$)	6 ($3A_1$, 3E)
Infrared–Raman coincidences	3 ($3E'$)	6 ($3A_1$, 3E)
Polarized Raman modes	2 ($2A_1'$)	3 ($3A_1$)
Stretches	4 ($2A_1'$, A_2'', E')	4 ($2A_1$, B_1, E)
Deformations	4 (A_2'', $2E'$, E'')	5 (A_1, B_1, B_2, 2E)

The vibrational spectra thus seem to provide substantive evidence that the coordination polyhedron in the pentacyclopropylantimony(V) molecule resembles that

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(17) Symmetry designations for the cyclopropyl–antimony vibrations are given in terms of the skeletal symmetry about the antimony atom here and in Table I.

(18) S. R. Leone, B. Swanson, and D. F. Shriver, *Inorg. Chem.*, 9, 2189 (1970).

(19) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 116.

(20) A. J. Downs, R. Schmutzler, and I. A. Steer, *Chem. Commun.*, 221 (1966).

(21) T. V. Long and F. R. Huege, *ibid.*, 1239 (1968).

of the corresponding pentaphenyl derivative, and it is square pyramidal. This suggests that the structure in both cases may be a result of electronic rather than environmental effects. Unfortunately, both ^{13}C nmr and ^{1}H resonance measurements utilizing a 100-MHz instrument (30°)[22] indicate that this molecule is a stereochemically nonrigid system on a magnetic resonance time scale,[23] and they provide no other information concerning the molecular structure. This is not unexpected since, as Muetterties points out, "All ML_5 molecules investigated by nmr have shown apparent magnetic equivalence of ligand nuclei."[23] The relatively clear-cut assignment of the vibrational spectrum of this molecule utilizing C_{4v} point group selection rules presumably indicates that the ground-state lifetime is long with respect to the vibrational time scale.[24]

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(22) Private communication from Professor George Gray of the Oregon Graduate Center. The natural-abundance ^{13}C spectrum taken at 40 Hz/sec on a 1000-Hz sweep showed but two bands with an intensity ratio 55:27 ($\sim$2:1), presumably reflecting the ratio of methylene to methyne carbons in the cyclopropyl rings. Although it is possible that this ratio arises because the shifts associated with carbon atoms in structurally nonequivalent cyclopropyl rings of either a C_{4v} or a D_{3h} polyhedron are accidentally degenerate, it seems more likely that the magnetic equivalence arises from structural nonrigidity (see Discussion). Two complex multiplets separated by *ca.* 70 Hz, each of total width 50 Hz, appear in the proton resonance spectrum, and the multiplet intensity ratio is 3:2. Since the ^{13}C spectrum, which should be more sensitive to the molecular symmetry features than the ^{1}H spectrum, indicates that the five ligating carbon nuclei are magnetically equivalent, the proton multiplet ratio is assumed to be the ratio of protons on the opposite side of the cyclopropyl ring from the Sb atom to those on the same side. We appreciate Professor Gray's interest in this problem and his courtesy in informing us of his experimental results.

(23) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965); *Accounts Chem. Res.*, **3**, 266 (1970).

(24) If the traverses of polytopal forms were rapid on a vibrational time scale, then the Raman and infrared selection rules would be determined using a treatment similar to those involving the permutational symmetry groups discussed by Longuet-Higgins.[25] To our knowledge, a treatment of this sort applicable to the nonrigid behavior in question is not available in the literature.

(25) H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963).

Ligand Binding by Metalloporphyrins. II. The Effect of Solvent on the Thermodynamic Functions

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Abstract: The study of free energy, enthalpy, and entropy changes accompanying the addition of substituted pyridines to iron(II) porphyrins has been extended to follow the effect of solvent change on these thermodynamic functions. Free energy changes are an unreliable index of strength of binding, but very large solvent effects are observed for enthalpy and entropy changes. Enthalpy effects were most favorable and entropy effects least favorable in carbon tetrachloride with decreasing magnitudes in chloroform and benzene. Statistical treatment of the results (62 data pairs) suggests that the contributions to these thermodynamic functions from different solvents, ligands, and metalloporphyrins operate independently and are additive. A linear model is proposed which simulates these effects. The thermodynamic data may be rationalized in terms of a relaxation in the binding of solvent molecules by heme when ligands are attached. The types of heme–solvent interaction occurring in the three solvents are different and solvation energies appear to decrease in the order benzene > chloroform > carbon tetrachloride. The associated large entropy changes follow the same order.

Because the binding of ligands by metalloporphyrins is of interest to both chemists and biochemists, numerous stability constant measurements and studies of the free energy of reaction have been carried out.[2]

In our previous study[3] the thermodynamic functions for the addition of pyridine ligands to iron(II) porphyrins were determined as ligand and porphyrin were varied. The free energies of reaction varied over a wide range (-1.8 to -9.0 kcal mol^{-1}) and the changes in enthalpy and entropy of reaction were unexpectedly large. It is apparent that the iron(II) porphyrin–pyridine system is very sensitive to substitutions in the porphyrin and the ligand and that the study of enthalpy and entropy changes as well as free energy changes is essential to any understanding of these substituent effects.

It is well known that the ligand-addition reactions of the protein-bound iron porphyrins are greatly influenced by the heme environment. Only in this way can the great changes in reactivity of the different protohemin–protein complexes, *e.g.*, catalase, cyto-

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(2) (a) J. R. Miller and G. D. Dorough, *J. Amer. Chem. Soc.*, **74**, 3977 (1952); (b) J. E. Falk in "Porphyrins and Metalloporphyrins," Elsevier, New York, N. Y., 1964, p 45.

(3) S. J. Cole, G. C. Curthoys, and E. A. Magnusson, *J. Amer. Chem. Soc.*, **92**, 2991 (1970).