yet reported and the only Sn–C distance reported for an octahedrally coordinated tin atom. The sum of the covalent radii[13] for Sn and C is 2.17 A which agrees quite well with the average observed distance (2.16 ± 0.02 A) for the other compounds given in Table IV. The Sn–C distance (2.16 A) in the trigonal bipyramidal $(CH_3)_3SnCN$ is within experimental error equal to that (2.14–2.18 A) observed for the tetrahedral tin compounds which constitute the remainder of the examples in Table IV. Although it is possible that the change in the nature of the hybrid orbitals on Sn may cause the octahedral Sn–C bond length to be different from the tetrahedral and trigonal bipyramidal bond lengths, the short bond length observed here for Sn–C is probably due to the highly ionic character of the $(SnF_2)_\infty$ sheet. The resulting positive charge on Sn leads to increased ionic character in the Sn–C bond and thus to a shorter bond length.

It is interesting that the bridging Sn–F distance is 0.1 A shorter in SnF_4 than in $(CH_3)_2SnF_2$. It seems reasonable to describe the structures in the first approximation as $Sn^{4+}[F^-]_4$ and $(CH_3)_2Sn^{2+}[F^{-1}]_2$. Using the univalent crystal radii of Pauling,[14] one can estimate that the crystal radius of Sn^{4+} ought to be about 0.12 A shorter than that of Sn^{2+}. This agrees well with the difference found.

A detailed discussion of the bond lengths and bonding will be deferred until the results of structural studies of $(C_6H_5)_2SnF_2$ and another dialkyltin difluoride are available.

[13] See ref 10, pp 224–229.

[14] See ref 10, p 514.

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The Infrared Spectra and Structure of Some Trimethylantimony Derivatives, $(CH_3)_3SbX_2$

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The compounds $(CH_3)_3SbX_2$ where X^- (or X^{2-}) is F^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, CrO_4^{2-}, and $C_2O_4^{2-}$ have been prepared, and their infrared spectra in the 200–4000 cm^{-1} region have been observed. The latter show that, in the anhydrous compounds, free anions are not present, and comparisons are best drawn with the spectra of related covalent species. For example, the infrared spectrum of trimethylantimony carbonate is very similar to that of dimethyl carbonate. Attempts to prepare $(CH_3)_3Sb(BF_4)_2$ and $(CH_3)_3SbSiF_6$ gave impure products containing trimethylantimony difluoride, and BF_3 and SiF_4 were liberated. The evidence thus indicates that strong coordinative interactions occur between $(CH_3)_3Sb$ and X in all these compounds, leading to nonionic, five-coordinate structures, and in some cases to breakdown of the anionic group.

Introduction

Trialkylantimony(V) derivatives, R_3SbX_2, have been investigated by several workers who have established the widespread occurrence of the trigonal bipyramidal structure. Wells[2] showed that trimethylantimony dichloride, dibromide, and diiodide are isomorphous and have a trigonal bipyramidal structure with a planar $(CH_3)_3Sb$ group and the halogens at the apices. Triphenylantimony dibromide has recently been shown to have the same structure,[3] in agreement with the conclusions reached by Jensen,[4] on the basis of dipole moment determinations. More recently, Long, Doak, and Freedman have made infrared spectroscopic studies[5] of some trimethylantimony(V) derivatives and have concluded that trimethylantimony dinitrate is an ionic solid, $[(CH_3)_3Sb]^{2+}$ $(NO_3)_2^{2-}$, and that in the analogous sulfate, $(CH_3)_3SbSO_4$, the sulfate groups are covalently bonded.

In view of the numerous studies of triorganotin derivatives which establish the nonionic, solid-state structures of trimethyltin fluoride,[6] trimethyltin nitrate,[7,8] trimethyltin perchlorate,[7] dimethyltin chromate,[9] and related organotin derivatives, the related question of the existence of R_3Sb^{2+} ions in the solid state is an obvious one. There is certainly no apparent reason for the structural difference between trimethylin nitrate[7,8] and trimethylantimony dinitrate, as reported by Doak, *et al.*[5] We have therefore reinvestigated the infrared spectrum of trimethylantimony dinitrate and have similarly examined a number of other trimethylantimony(V) derivatives to provide a more extensive comparison with the analogous organotin compounds.

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[2] A. F. Wells, *Z. Krist.*, **99**, 367 (1938).

[3] T. N. Polynova and M. A. Porai-Koshits, *J. Struct. Chem.* (USSR) **1**, 146 (1960).

[4] K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **250**, 268 (1943).

[5] G. G. Long, G. O. Doak, and L. D. Freedman, *J. Am. Chem. Soc.*, **86**, 209 (1964).

[6] H. C. Clarke, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, 2332 (1964).

[7] (a) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 740 (1963); (b) R. Okawara, B. J. Hathaway, and D. E. Webster, *Proc. Chem. Soc.*, 13 (1963).

[8] H. C. Clark, R. J. O'Brien, and A. L. Pickard, *J. Organometal. Chem.*, **4**, 43 (1965).

[9] H. C. Clark and R. G. Goel, *Inorg. Chem.*, **4**, 1428 (1965).

TABLE I

ANALYTICAL DATA

Compd	Solvent (for prep)	Calcd		Found		Hydrolyzed
		C, %	H, %	C, %	H, %	
$(CH_3)_3SbF_2$	Aqueous HF	17.58	4.39	17.00	4.29	No
$(CH_3)_3Sb(NO_3)_2$	Anhyd CH_3OH	12.40	3.10 (N, 9.63)	12.78	2.95 (N, 9.89)	Slowly
$(CH_3)_3SbCO_3$	SO_2	21.17	4.00	21.37	4.23	No
$(CH_3)_3SbSO_4$	H_2O	13.70	3.45	13.78	3.87	No
$(CH_3)_3SbCrO_4$	H_2O	12.73	3.20 (CrO_4, 41.03)	12.66	3.12 (CrO_4, 41.29)	No
$(CH_3)_3SbC_2O_4$	H_2O	23.55	3.56	23.51	3.68	No

Experimental Section

General.—Except where preparations were performed in aqueous solutions, all manipulations were carried out in a nitrogen-filled drybox. Conventional vacuum techniques were used for the manipulation of volatile substances, and a modified form of an apparatus described by Parry, Schultz, and Giradot[10] was used for carrying out reactions in liquid sulfur dioxide. Microanalyses for C, H, N, and F were done in the microanalytical laboratory of this department, at the Microanalytisches Laboratorium, Max-Planck-Institut, Mülheim, Germany, or at the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Boron and chlorine analyses were obtained through the courtesy of Dr. E. L. Muetterties, who also provided the sample of $Ag_2B_{12}Cl_{12}$.

Infrared spectra in the range 700–4000 cm^{-1} were recorded on a Perkin-Elmer Model 21 spectrophotometer, and spectra in the 200–2000 cm^{-1} range on a Perkin-Elmer Model 421 grating spectrophotometer. Perkin-Elmer Model 137 Infracords fitted with sodium chloride or potassium bromide optics were also used. Samples were generally prepared in the drybox as mulls in Nujol, hexachlorobutadiene, or halocarbon oil and then placed between plates of cesium iodide, potassium bromide, or 1.0-mm sheets of silver chloride or polyethylene. The samples were protected from moisture by wrapping polyvinyl tape around the plates. Spectra of the dinitrate, carbonate, sulfate, chromate, and oxalate were also recorded in potassium bromide pellets using freshly dried potassium bromide. Several spectra of each substance were recorded at different concentrations, and spectra were also recorded after exposing the compound to air. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer using quartz cells.

X-Ray powder photographs were taken with a 14.32-cm diameter camera, using copper Kα radiation with a nickel filter on a G.E. X-ray unit. Quartz capillary sample tubes of either 0.5- or 0.3-mm diameters were filled in the drybox and sealed.

Trimethylantimony Dibromide.—This was prepared by the method of Morgan and Davies,[11] using freshly distilled Analar grade antimony trichloride and methylmagnesium iodide. The trimethylstibine and ether were codistilled in a nitrogen atmosphere, and the distillate was treated with a carbon tetrachloride solution of bromine. Precipitated trimethylantimony dibromide was filtered off and recrystallized from water. *Anal.* Calcd for $C_3H_9SbBr_2$: C, 11.20; H, 2.80; Br, 48.92. Found: C, 11.09; H, 2.46; Br, 48.90.

Trimethylantimony difluoride, dinitrate, carbonate, sulfate, chromate, and oxalate were prepared by reaction of the bromide with the corresponding silver salt. Details are given in Table I.

The fluoride and nitrate are soluble in water, methanol, and chloroform; the carbonate is soluble in water and methanol but not chloroform, while the sulfate, chromate, and oxalate are soluble in water but not in methanol, acetone, or acetonitrile.

Trimethylantimony Bis(perchlorate).—From the reaction of trimethylantimony dibromide and silver perchlorate in anhydrous methanol, a white anhydrous solid was obtained which exploded violently and readily. Further work was not carried out.

Trimethylantimony Bis(tetrafluoroborate).—Trimethylantimony dibromide (0.561 g) and silver tetrafluoroborate (1.027 g) were allowed to react in 25 ml of anhydrous methanol. After removal of the precipitated silver bromide and of the solvent, a white solid was obtained which sublimed under vacuum at 50°. The analytical results of both the sublimed and unsublimed products were identical. *Anal.* Calcd for $C_3H_9SnB_2F_8$: C, 10.47; H, 2.66. Found: C, 14.28; H, 3.60. Some decomposition had apparently occurred and this was supported by the fact that X-ray powder photographs of the sublimed solid showed the presence of trimethylantimony difluoride. The methanol recovered from the original preparation was highly acidic and contained boron trifluoride. The latter was identified by the infrared spectrum of the solution and by positive qualitative tests for boron and fluorine. The infrared spectra of samples of the sublimed solid which had been exposed to air showed the characteristic absorption band of the BF_4^- ion at 1055 cm^{-1}.

Trimethylantimony Hexafluorosilicate.—Trimethylantimony dibromide (1.016 g) and silver hexafluorosilicate (1.113 g) were allowed to react in 25 ml of anhydrous methanol, and a colorless, deliquescent, crystalline solid was obtained after removal of the methanol as described above. The solid was sublimed under vacuum at 50°, and both the unsublimed and sublimed solids gave identical infrared spectra and analytical results. *Anal.* Calcd for $C_3H_9SbSiF_6$: C, 11.65; H, 2.93; F, 36.90. Found: C, 14.99; H, 3.71; F, 28.00. X-Ray powder photographs of the sublimed solid showed the presence of trimethylantimony difluoride. The infrared spectrum of a sample exposed to air showed the characteristic absorption bands of the SiF_6^{2-} ion at 735 and 480 cm^{-1}. The recovered methanol was highly acidic and gave positive tests for both silicon and fluorine.

Trimethylantimony Bis(hexafluoroantimonate). (a).—Trimethylantimony dibromide (0.724 g) and silver hexafluoroantimonate (1.524 g) were allowed to react in 25 ml of anhydrous methanol. The silver bromide was filtered off, and most of the methanol was removed under vacuum at 25°. The last traces of methanol could not be removed even on prolonged pumping at 100°. Moreover, the recovered methanol did not show any acidity and gave negative tests for fluoride and antimony.

(b).—The metathetical reaction of trimethylantimony dibromide (1.108 g) and silver hexafluoroantimonate (2.330 g) in 25 ml of liquid sulfur dioxide gave, following the removal of the precipitated silver bromide and evaporation of the sulfur dioxide, an extremely hygroscopic white solid. *Anal.* Calcd for $C_3H_9Sb_3F_{12}$: F, 35.72. Found: F, 30.90. X-Ray powder photographs of the solid did not show any lines due to trimethylantimony difluoride.

Trimethylantimony Derivative of $B_{12}Cl_{12}^{2-}$.—Trimethylantimony dibromide (0.332 g) and $Ag_2B_{12}Cl_{12}$ (0.784 g) were allowed to react in anhydrous methanol. After the silver bromide had been filtered off, a colorless solution remained which, on evaporation under vacuum at 25°, gave a pinkish red solid which from its infrared spectrum still contained some methanol. The recovered methanol was not acidic and gave negative tests for boron and chlorine. The reddish solid was then heated at approximately 60° under vacuum for 6 hr. *Anal.* Calcd for C_3H_9-

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(10) R. W. Parry, D. R. Schultz, and P. R. Girardot, *J. Am. Chem. Soc.*, **80,** 1 (1958).

(11) G. T. Morgan and G. R. Davies, *Proc. Roy. Soc.* (London), **A110,** 523 (1926).

$SbB_{12}Cl_2$: B, 17.9; Cl, 58.9. Calcd for $C_3H_9SbB_{12}Cl_{12}(CH_3OH)$: B, 17.3; Cl, 56.4. Found: B, 17.3; Cl, 56.0. However, the infrared spectrum of the heated solid did not show any absorption bands due to methanol, nor were better analytical results obtained after further heating under vacuum. The compound dissolved in water or methanol to give a colorless solution, but evaporation of these solutions always gave the same pinkish red solid.

Discussion

Although the trigonal bipyramidal structures of trimethylantimony dichloride, dibromide, and diiodide have been established crystallographically,[2] similar studies have not been made of the difluoride. Moreover, Long, *et al.*,[5] reported that the difluoride, in addition to the infrared bands associated with the $(CH_3)_3Sb$ group, showed complex bands at 1120–1050, 730, and 540–450 cm^{-1}, the latter partially masking the Sb–C asymmetric stretching frequency at 586 cm^{-1}. They therefore could not relate the fluoride to the structures of the other dihalides. We have reexamined the spectrum of the difluoride and do not observe any of the above complex bands. The observed frequencies were 3065 (w) and 2965 (w) (C–H stretch), 2450 (vw), 2110 (vw), 1812 (w), 1768 (w), 1415 (m) (CH_3 asymmetric bend), 1235 (m) and 1221 (m) (CH_3 symmetric bend), 855 (vs) (CH_3 rock), 585 (s) (Sb–C asymmetric stretch), and 475 (vs) (Sb–F asymmetric stretch) cm^{-1}. The spectrum is therefore consistent with a trigonal bipyramidal structure, and the covalent nature of the difluoride is further indicated by the fact that it sublimes at room temperature under vacuum (10^{-3} mm pressure) and by its solubility in methanol, acetone, and chloroform. A comparison can also be made of the Sb–F stretching frequency in trimethylantimony difluoride (475 cm^{-1}) with the band we have now observed at 355 cm^{-1} for trimethyltin fluoride and assigned to the Sn–F stretching frequency.

Table II

Infrared Data for $(CH_3)_3Sb(NO_3)_2$ and $(CH_3)_3SbCO_3$

$(CH_3)_3Sb(NO_3)_2$[a]	$(CH_3)_3SbCO_3$[b]	Assignment
3070 m	2950 m	CH asym str
2960 m	2880 sh	CH sym str
	1730 s	ν_1 C–O str
1530 s, br		ν_4 NO_2 asym str
1415 m	1395 w	CH asym bend
1290 s		ν_1 NO_2 sym str
1275 s	1280 s	*and*
1245 m		ν_4 CO_2 asym str
1230 m	1225 m	CH sym bend
965 s	1115 s	ν_2 NO str
	1100 s	ν_2 CO_2 sym str
865 s	875 s	CH_3 rock
795 m	790 s	ν_6 MO_3 out-of-plane def
728 s	740 s	ν_3 MO_2 sym bend
708 m	632 s	ν_5 MO_2 asym bend
580 s	575 s	Sb–C asym str
520 w, br	525 w	Sb–C sym str *or*
	510 w	Sb–O str
	450 m	Sb–O str
	375 m	*or*
	250 s	lattice modes

[a] The nitrate shows additional weak bands at 2820, 2260, 1990, 1820, 1765, and 1675 cm^{-1}. [b] The carbonate shows additional weak bands at 1460, 1075, and 1040 cm^{-1}. s, strong; m, medium; w, weak; br, broad; sh, shoulder.

Trimethylantimony Dinitrate.—For trimethylantimony nitrate, Long, *et al.*,[5] report nitrate absorption frequencies at 1516 (s), 1457 (s), 1050 (vw), 834 (s), and 728 (w) cm^{-1}. However, these workers made no attempt to exclude moisture rigorously, and although their analytical data agree with the values required for the dinitrate, we have found that reliable spectra could only be obtained under carefully controlled conditions. The nitrate was prepared in anhydrous methanol and completely reproducible spectra were recorded using Nujol mulls placed between silver chloride sheets. When potassium bromide plates were used, or when the sample was prepared as a potassium bromide pellet, considerable exchange occurred. The absorption frequencies of trimethylantimony dinitrate, together with relative intensities and suggested assignments, are listed in Table II. The absorption bands due to the nitrate group clearly show the features expected for a nitrato, $-ONO_2$, group as opposed to a free nitrate ion, namely (i) the strong band at 965 cm^{-1}, assigned as ν_2 and usually observed[12] in the 950–1050 cm^{-1} region; (ii) the low frequency (795 cm^{-1}) of the out-of-plane rocking mode (ν_6);[13] and (iii) the magnitude of the splitting ν_4–ν_1, in this case approximately equal to 260 cm^{-1}. The magnitude of this splitting has been suggested[14] as a criterion of the strength of the nitrato covalent bond, and Katzin[15] has concluded that a ν_4–ν_1 splitting greater than 125 cm^{-1} is undoubtedly due to partial covalent bonding.

The bands arising from the trimethylantimony group show the expected features, in particular the presence of the medium to strong intensity band at 580 cm^{-1} assigned to the Sb–C asymmetric stretching frequency. This is in agreement with a planar $(CH_3)_3Sb$ group, although the weak band at 520 cm^{-1} may be the Sb–C symmetric stretching frequency. Long, *et al.*,[5] observed a weak band at 528 cm^{-1} in the infrared spectra of $[(CH_3)_3SbCl]_2O$ and $[(CH_3)_3SbClO_4]_2O$, which they suggested may be associated with the Sb–O stretching vibration or may be the Sb–C symmetric stretching frequency arising from a distortion of the planar $(CH_3)_3Sb$ group. Very recently, Cullen, Deacon, and Green[16] observed the infrared-forbidden Sb–C symmetric stretch as a weak band at 529 cm^{-1} in the infrared spectrum of $[(CH_3)_4Sb]HgI_3$. The weak band at 520 cm^{-1} in the spectrum of trimethylantimony dinitrate and similar bands at 520–530 cm^{-1} in the spectra of trimethylantimony carbonate and chromate may therefore be due to Sb–O stretching vibrations, but assignment to the Sb–C symmetric stretching vibration, appearing as a symmetry-forbidden mode or because of a slight distortion from planarity, cannot be overlooked. The spectrum of trimethylantimony dinitrate

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[15] L. I. Katzin, *J. Inorg. Nucl. Chem.*, **24**, 245 (1962).

[16] W. R. Cullen, G. B. Deacon, and J. H. S. Green, *Can. J. Chem.*, **43**, 3193 (1965).

is therefore consistent with a trigonal bipyramidal structure in which unidentate nitrato groups occupy the apical positions about the planar $(CH_3)_3Sb$ group.

Further evidence of partial covalent bonding in trimethylantimony dinitrate is provided by the ultraviolet absorption spectrum. In aqueous solutions of the dinitrate, the absorption maximum occurs at 302 mμ, and in chloroform solution at 280 mμ. The former is characteristic of the free nitrate ion and is attributed to the symmetry-forbidden $n \rightarrow \pi^*$ transition.[17] That this transition should occur at 280 mμ in chloroform solution is in agreement with observations on transition metal nitrates[18] and dimethyltin dinitrate,[19] where covalently bonded nitrato groups occur.

Trimethylantimony Carbonate.—The observed absorption frequencies, with their relative intensities and suggested assignments, are shown in Table II. The bands associated with $(CH_3)_3Sb$ occur at the frequencies expected and are consistent with a planar geometry, although there is uncertainty over the assignment of bands in the 450–550 cm^{-1} region. Bands which can be attributed to the carbonate group occur at 1730, 1280, 1115, 1100, 790, 740, 632, 450, 375, and 250 cm^{-1}. The weak bands at 1460, 1075, and 1040 cm^{-1} are probably overtones and combination bands. The carbonate bands clearly show that the carbonate group is involved in partial covalent bonding[20] and that its symmetry cannot be higher than C_{2v}. The splitting of the doubly degenerate ν_3 mode, for the free ion, observed in ionic carbonates at 1415 cm^{-1}, into two well-defined bands at 1730 and 1280 cm^{-1}, is too large to be attributed to crystal field effects.[21] In fact, these frequencies can be compared with those observed at 1750 and 1280 cm^{-1} in the spectrum of dimethyl carbonate.[22] Similarly, the Raman-active mode ν_1 of the free ion appears as an intense band, split into a doublet at 1115 and 1100 cm^{-1}; the corresponding band in dimethyl carbonate occurs at 965 cm^{-1}, and at 1078 cm^{-1} in solid ethylene carbonate.[23] The other degenerate mode ν_4 of the free ion has split into two strong bands at 740 and 632 cm^{-1}, and the out-of-plane mode ν_2 of the free ion shows a strong absorption at 790 cm^{-1}. The bands at 450, 375, and 250 cm^{-1} are similar to those observed for dimethyltin carbonate[24] and may be due to lattice modes. Miller, *et al.*,[25] have reported similar bands in the spectra of some metal carbonates; *e.g.*, lithium carbonate absorbs at 498 and 420 cm^{-1} and lead (II) carbonate at 400 cm^{-1}. The infrared spectrum of trimethylantimony carbonate can best be interpreted in terms of a polymeric structure in which each carbonato group functions as a bridge through two of its oxygen atoms to presumably planar trimethylantimony groups. The other possible arrangement in which a carbonato group is bonded to two corners of a trigonal bipyramidal monomer would require either a nonplanar $(CH_3)_3Sb$ group (and hence a much more intense Sb–C symmetric stretching absorption) or a highly strained bidentate carbonato group occupying two *trans* positions.

Trimethylantimony Sulfate.—Long, *et al.*,[5] concluded, from its infrared spectrum, that trimethylantimony sulfate is covalent, although they reported that the infrared bands do not agree well with those of sulfato complexes and that complete interpretation of the spectrum was difficult. They also reported that pronounced changes occurred in the spectrum when the sample, as a potassium bromide pellet, was exposed to the atmosphere. Our results, shown in Table III, agree well with those of Long, *et al.*[5] Bands associated with the trimethylantimony group are those expected, although the Sb–C asymmetric stretching vibration was not observed and was apparently masked by the strong sulfate peak at 600 cm^{-1}.

TABLE III

INFRARED DATA FOR $(CH_3)_3SbSO_4$ AND $(CH_3)_2SO_4$

$(CH_3)_3SbSO_4$[a]	$(CH_3)_2SO_4$[b]	Assignment
3050 w	3100 m	C–H str
2950 w		
1415 m		CH asym bend
1285 s	1395 s	ν_6 SO_2 asym str
1230 m		CH sym bend
1145 s	1200 s	ν_1 SO_2 sym str
950 s	825 s	ν_8 SO_2[c] asym str
860 s		CH_3 rock
825 s	752 s	ν_2 SO_2[c] sym str
650 s	592 m	ν_7 SO_4 rock
600 s	573 m	ν_3 SO_2 bend
495 m	502 s	ν_9 SO_4 rock
428 w	428 m	ν_4 SO_2[c] bend
250 s		Lattice mode

[a] Additional weak bands at 2120, 1760, and 980 cm^{-1}. [b] Additional bands at 1460, 1010, 985, 615, and 520 cm^{-1}. [c] Denotes oxygen atom involved in bonding. s, strong; m, medium; w, weak.

The number of sulfate absorption bands clearly shows the free SO_4^{2-} ions are not present and that the symmetry of the sulfate group[5] cannot be higher than C_{2v}. It is true that the observed frequencies do not correspond well with those reported[26] for metal sulfato complexes containing unidentate or bidentate sulfate groups, but, in agreement with the spectral similarities of trimethylantimony carbonate and dimethyl carbonate, a reasonable comparison can be made of the sulfate with dimethyl sulfate. The spectrum of dimethyl sulfate has been reported previously,[27] although not in the 40–650 cm^{-1} region. Our results, shown in Table III, agree with the earlier data, except that, whereas Detoni and Hadzi[27] reported a band at 875 cm^{-1} which they assigned as the O–S–O asymmetric stretching frequency, we find no band at 875

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(19) C. C. Addison, W. B. Simpson, and A. Walker, *J. Chem. Soc.*, 2360 (1964).

(20) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *ibid.*, 3137 (1958).

(21) S. D. Ross and J. Goldsmith, *Spectrochim. Acta*, **20**, 781 (1964).

(22) J. L. Hales, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, 618 (1957).

(23) C. L. Angel, *Trans. Faraday Soc.*, **52**, 1178 (1956).

(24) R. G. Goel, Ph.D. Thesis, University of British Columbia, 1965.

(25) F. A. Miller, G. L. Carlson, F. F. Bentley, and W. H. Jones, *Spectrochim. Acta*, **16** 135 (1960).

(26) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957).

(27) S. Detoni and D. Hadzi, *Spectrochim. Acta*, **11**, 601 (1957).

cm^{-1} but do observe one at 825 cm^{-1}. The absorption frequencies in the 400–650 cm^{-1} region have been assigned from a comparison with the spectrum of sulfuryl difluoride.[28]

Although the separations of the four sulfate bands of trimethylantimony sulfate at 1285, 1145, 905, and 825 cm^{-1} are less than those among the corresponding four bands at 1395, 1200, 825, and 752 cm^{-1} of dimethyl sulfate, they are very much greater than those observed for metal–sulfato complexes. Moreover, there is a general similarity in the pattern of the infrared bands of the antimony compound and dimethyl sulfate, and the assignments given in Table III were made on this basis. The only band not readily assigned is at 250 cm^{-1}; this is possibly a lattice mode. It is evident from the spectrum that trimethylantimony sulfate is largely covalent and probably has a polymeric structure containing bridging sulfato groups, each being bonded through two oxygen atoms to two trimethylantimony groups.

When a potassium bromide pellet containing trimethylantimony sulfate was exposed to the atmosphere, changes were observed in the infrared spectrum after about 4 hr. Additional bands due to ionic sulfate and a new band at 565 cm^{-1} were observed. These changes were most probably due to the exchange reaction between potassium bromide and the sulfate, and not due to hydrolysis, since no spectroscopic changes were observed for a sample of the anhydrous trimethylantimony sulfate exposed to the atmosphere for 24 hr. Certainly the peak at 565 cm^{-1} can be assigned to the Sb–C asymmetric stretching vibration of trimethylantimony dibromide.

Trimethylantimony Chromate.—The infrared spectrum of trimethylantimony chromate showed absorptions attributable to the $(CH_3)_3Sb$ group at 3040 (CH asymmetric stretch), 2940 (CH asymmetric stretch), 1410 (CH_3 asymmetric bend), 1230 (CH_3 symmetric bend), 852 (CH_3 rock), and 575 (Sb–C asymmetric stretch) cm^{-1}. A weak band at 530 cm^{-1} may be assigned to the Sb–C symmetric stretch, suggesting that the trimethylantimony group may not be completely planar, or alternatively to an Sb–O vibration as in the analogous carbonate and nitrate. Absorption bands due to the chromate group occur at 964 (s), 940 (s), 838 (s, br), 700 (s, br), 420 (m), 390 (m), 355 (m), and 313 (m) cm^{-1}. These are almost identical with those observed for dimethyltin chromate[9] and clearly show that the symmetry of the CrO_4 group cannot be higher than C_{2v}. The spectrum is again consistent with a polymeric structure similar to that proposed for trimethylantimony sulfate.

Trimethylantimony Oxalate.—The observed frequencies and the suggested assignments for trimethylantimony oxalate are shown in Table IV. The bands associated with $(CH_3)_3Sb$ are readily assigned and agree with those observed for the above compounds. For this compound also, a band is observed in the 525 cm^{-1} region, although in this case it is certainly due to a vibration of the oxalate group. The fact that the Sb–C asymmetric stretching vibration appears in the same frequency region and with almost the same intensity as in trimethylantimony dibromide indicates that the geometry of the trimethylantimony group does not differ significantly in the two compounds.

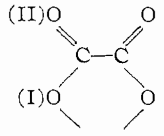
TABLE IV

INFRARED FREQUENCIES (CM^{-1}) OF TRIMETHYLANTIMONY OXALATE

3035	w[a]	CH asym str	855	s	CH_3 rock
2950	m	CH sym str	827	s, sh	C–C str (A_1)
2570	w		755	s	O(I)–C–O(II) asym bend (B_1)
1665	vs	C–O(II) str (B_1)			
1620	s, sh	C–O(II) str (A_1)	585	w	C–C–O asym bend (B_1)
1375	m	C–O(I) str (A_1)	575	m	Sb–C asym str
1250 1227 1215	vs	C–O(I) str (B_1)	525	s	C–C–O sym bend (A_1)
			420	s	O(I)–C–O(II) sym bend (A_1)

[a] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

To assign the oxalate bands, comparisons can be made with the infrared bands reported for the oxalate ion, for metal–oxalato complexes, and for *cis*-dimethyl oxalate. Assignments of the fundamental frequencies of the oxalate ion have been reported by several workers,[29–31] but there are several disagreements notably on whether the symmetry is V_h or V and on the assignments of some low-frequency bands. Since our observations of the infrared spectrum of sodium oxalate are entirely in agreement with those of Fujita, *et al.*,[30] the assignments of these authors are used in the following discussion. In metal–oxalato complexes and *cis*-dialkyl oxalates, the symmetry of the oxalate group is lowered to C_{2v} as in the diagram. A normal coordinate analysis of metal–oxalato complexes has been completed,[32] as well as complete structural determinations of complexes[33] such as $K[Cr(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$. It is therefore well established that the frequencies of the C–O(II) stretching vibrations (1700–1600 cm^{-1}) increase and those of the C–O(I) stretching vibrations (1450–1350 cm^{-1} and 1300–1200 cm^{-1} regions) decrease as the frequency of the metal–oxygen stretching vibration increases. In *cis*-dimethyl oxalate, where the O(I) atoms are covalently bonded to CH_3 groups, the C–O(II) and C–O(I) stretching frequencies appear[31] at 1776, 1770, and 1325, 1165 cm^{-1}, respectively.



The infrared bands due to the oxalate group of tri-

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methylantimony oxalate are clearly very different from those of the free oxalate ion[30] and are completely in accord with the oxalato group having C_{2v} symmetry. Thus, the bands at 1665 and 1250–1215 cm^{-1} correspond to the C–O(II) and C–O(I) stretching frequencies observed in metal–oxalato complexes, and Raman-active modes of the free $C_2O_4^{2-}$ ion now appear with moderate or strong intensity. In view of the probable planarity of the $(CH_3)_3Sb$ group and the C_{2v} symmetry of the oxalate group, it is suggested that the latter act as bridging units in a polymeric structure making the Sb atoms five coordinate. In such an arrangement, coupling between the various vibrational modes of the oxalate group may not be so strong as in metal–oxalato complexes containing the chelate ring. This has been considered in arriving at the assignments shown in Table IV.

Other Trimethylantimony Derivatives.—Attempts to prepare the pure compounds $(CH_3)_3Sb(BF_4)_2$ and $(CH_3)_3SbSiF_6$ were unsuccessful, and the products were always approximately 1:1 mixtures of trimethylantimony difluoride and the desired derivative. Decomposition to the difluoride must accompany the removal of solvent, *e.g.*

$$(CH_3)_3Sb^{2+}\text{ (solvated)} + 2BF_4^- \underset{}{\overset{-CO_3OH}{\rightleftarrows}} (CH_3)_3SbF_2 + 2BF_3$$

Moreover, the infrared spectra of these mixtures did not show the features expected for the BF_4^- and SiF_6^{2-} ions. For the tetrafluoroborate mixture, bands were observed at 1287 (m), 1150 (sh), 1100 (s), 1053 (s), 1040 (sh), 1015 (sh), 760 (w), 572 (s), 545 (w), 515 (m), and 400 (s, vb) cm^{-1}, suggesting C_{3v} symmetry[34] of the BF_4 units. Similarly, the hexafluorosilicate mixture showed bands attributable to the SiF_6 group at 1495 (m), 1288 (m), 1057 (w), 997 (s), 785 (s), 720 (m), 555 (s), 533 (w), 445 (m), and 350 (m) cm^{-1} and not the two peaks at 726 (ν_3) and 480 (ν_4) cm^{-1} expected for the SiF_6^{2-} ion.[35] Both the anionic decompositions and the spectroscopic data reveal the strong interaction between $(CH_3)_3Sb$ and BF_4^- or SiF_6^{2-}.

Similarly, attempts to prepare $(CH_3)_3SbSbF_6$ and $(CH_3)_3SbB_{12}Cl_{12}$ did not give analytically pure compounds, although the products did not contain trimethylantimony difluoride or dichloride. For the hexafluoroantimonate product, the infrared bands at 1180, 665, 640, 550, 445, and 390 cm^{-1} were very similar to those observed for trimethyltin hexafluoroantimonate[36] although after exposure of the product to air the bands of the free SbF_6^- ion[35] were observed. For the $B_{12}Cl_{12}^{2-}$ product, the observed bands at 1030 (vs), 1000 (m), 827 (s), 532 (vs), 450 (m, br), and 320 (m) cm^{-1} differed considerably from those of the free $B_{12}Cl_{12}^{2-}$ ion.[37]

In conclusion, our results demonstrate the existence of an intense interaction between the $(CH_3)_3Sb$ group and the anions, X, in $(CH_3)_3SbX_2$ derivatives, and show that certain of these derivatives, *e.g.*, trimethylantimony carbonate, must be considered essentially covalent. All the infrared spectra show marked changes in absorption bands attributable to the anionic groups, *viz.*, significantly large splittings of degenerate modes and the appearance of Raman-active modes with medium to strong intensities. For reasons previously stated,[9] we do not consider that these spectroscopic observations can be explained in terms of just the low symmetry of the crystalline electrostatic field, particularly since these effects have now been observed through a broad spectrum of organotin and organoantimony compounds. An explanation requiring coordination of the anionic group with the organometallic residue seems much more likely.

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