

Fig. 2.— $J(^{119}\text{Sn}-\text{C}-\text{H})$ vs. Sn-C stretching frequencies for some methyltin compounds: 1, trimethyltin lithium (G. L. Morgan, Ph.D. Thesis, University of Illinois, 1962); 2, dimethyltin; 3, hexamethylditin; 4, tetramethyltin; 5, trimethyltin bromide^{21,22}; 6, trimethyltin chloride^{21,22}; 7, dimethyltin dichloride^{23,24}; 8, trimethyltin chloride (aqueous).^{21,22}

recently have presented evidence that the variation in ionic character of the bond may be of importance in affecting the Si-H coupling constant in substituted

silanes.²⁰ The relative constancy of the C¹³-H coupling constants²¹ in the compounds examined by Holmes and Kaesz does provide some assurance, however, that in the methyltin series hybridization change is of principal importance.

There is an interesting relationship between the observed Sn-CH₃ coupling constants and the symmetric and asymmetric (or degenerate) tin-carbon stretching frequencies, shown in Fig. 2. Data for methyltin halides are included.^{18,21,22} A linear relationship is evident for both vibrational modes.²³ Thus, the tin-carbon stretching frequencies are linearly related to the per cent s character in the tin orbital used in the bond, as measured by $J_{\text{Sn}-\text{CH}_3}$. The observed relationship provides strong indication that the Sn-C stretching force constant increases with increasing s character in the tin orbital. An analogous relationship between carbon orbital hybridization and the C-H force constant is well known.

The Sn-CH₃ rocking frequencies in the same series of compounds also increase with increasing value of the Sn-CH₃ coupling constant. The relationship is not, however, linear; the frequencies approach a constant upper limit with increasing value for the coupling constant.

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(20) C. S. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

(21) G. P. Van der Kelen, *Nature*, **193**, 1069 (1962).

(22) H. Kriegsmann and S. Pischtschan, *Z. anorg. allgem. Chem.*, **308**, 212 (1961).

(23) Interestingly, the line for the symmetric stretching frequency passes on extrapolation through the point 540 cm^{-1} , 98.5 c.p.s., the experimentally observed values for methyltin trichloride.^{21,24}

(24) R. Okawara, D. E. Webster, and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 3287 (1960).

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Trimethyltin Perchlorate, Trimethyltin Nitrate, and their Infrared Spectra

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Anhydrous trimethyltin perchlorate and trimethyltin nitrate have been prepared and both are volatile solids. The infrared spectrum of the perchlorate suggests that it is composed of planar trimethyltin groups bridged by partially covalent perchlorate groups to form chains. Trimethyltin nitrate, on the basis of its infrared spectrum, appears to contain a nitrate group linked to a non-planar trimethyltin group. Both the perchlorate and nitrate form diammonia adducts, which on the basis of their infrared spectra can best be formulated as $[(\text{CH}_3)_3\text{Sn}(\text{NH}_3)_2]^+\text{X}^-$, the tin atom having a trigonal bipyramidal configuration.

Recently, there has been considerable interest in the nature and constitution of organotin compounds and particularly of trialkyltin derivatives. Among the trialkyltin halides, interest arises from the marked physical and chemical differences between, say, tri-

methyltin fluoride and the remaining trimethyltin halides. Thus, such differences are taken to indicate that trimethyltin fluoride has a salt-like constitution, $(\text{CH}_3)_3\text{Sn}^+\text{F}^-$, while trimethyltin chloride, bromide, and iodide are thought to be molecular, crystalline solids.

Infrared spectroscopic evidence also suggests different structures for $(\text{CH}_3)_3\text{SnF}$ and $(\text{CH}_3)_3\text{SnCl}$. For compounds containing the $(\text{CH}_3)_3\text{Sn}$ group, the infrared spectra show one or two strong absorptions in the 500–600 cm^{-1} region. These have been assigned as the Sn–C symmetric and asymmetric stretching vibrations. If the three carbon atoms are trigonally planar with the tin atom, only the asymmetric vibration will be infrared active, and only one infrared band should be observed. Okawara, *et al.*,¹ observed only this one band for $(\text{CH}_3)_3\text{SnF}$, this being consistent with the ionic formulation, $(\text{CH}_3)_3\text{Sn}^+\text{F}^-$. For $(\text{CH}_3)_3\text{SnCl}$, two absorptions assigned to the symmetric and asymmetric Sn–C stretching vibrations are observed, in accord with a tetrahedral configuration about the tin atom and a covalent, molecular structure.

Similar infrared observations for the trimethyltin carboxylates have been interpreted also by Okawara, *et al.*,¹ in terms of ionic structures, *e.g.*, $(\text{CH}_3)_3\text{Sn}^+\text{OOCCH}_3^-$. However, Beattie and Gilson² point out that the spectroscopic evidence may equally well be interpreted in terms of either *bridging* acetate groups, or simple acetate *ions*. In the former case, trimethyltin acetate would presumably then consist of planar $(\text{CH}_3)_3\text{Sn}$ groups linked by bridging acetate groups, as described by Van Der Kerk, Luijten, and Janssen.³ The tin atom would be pentacoordinate and the structure could be considered as partially covalent. Since the acetate group is of low symmetry, such differences between the partially covalent and ionic models would not be expected to alter the selection rules and would therefore not be reflected spectroscopically. Similarly, trimethyltin fluoride may consist of planar $(\text{CH}_3)_3\text{Sn}$ groups separated by either fluoride ions or fluorine bridging atoms; in both cases the tin atom will be pentacoordinate. Very recently, trimethyltin hydroxide has been shown⁴ to have Sn–O–Sn bridges and hence five-coordination of the tin atoms.

To gain further information on the structure of triorgano tin compounds, we have prepared and examined by infrared spectroscopy trimethyltin perchlorate and trimethyltin nitrate. Both the ClO_4^- and NO_3^- ions are of high symmetry which will be markedly lowered should either of these groups function as bridging groups between planar $(\text{CH}_3)_3\text{Sn}$ moieties. Hathaway and Underhill⁵ have observed large changes in the infrared spectrum of the ClO_4 group produced by the lowering of symmetry when this group is involved in "partial covalent bond formation" to a cation. Similar studies have been made^{6,7} of the infrared spectra of the nitrate ion and of the coordinating nitrate group.

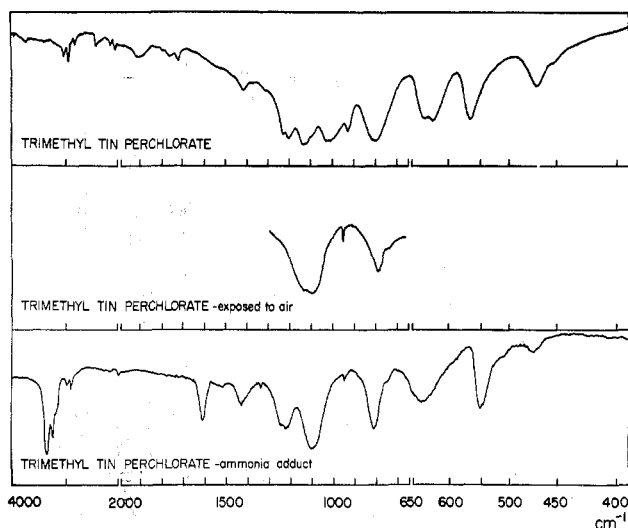


Figure 1.

Experimental

Compounds were prepared and handled in a nitrogen atmosphere in a drybox. Infrared spectra were determined using a Perkin-Elmer Model 21 double beam recording spectrophotometer, fitted with sodium chloride or potassium bromide optics. Samples were prepared usually as either Nujol or hexachlorobutadiene mulls.

Trimethyltin Perchlorate.—Anhydrous silver perchlorate (1.804 g., 8.69 mmoles) and trimethyltin bromide (2.117 g., 8.69 mmoles) were dissolved in dry methanol. Silver bromide (1.640 g., 8.73 mmoles) was filtered off, and most of the methanol removed under vacuum at room temperature. When about 3 ml. of methanol remained, the mixture solidified, but on further pumping melted again. The last traces of methanol were removed *in vacuo* at 120° to give a white crystalline solid which sublimed from the reaction flask. *Anal.* Calcd. for $\text{C}_3\text{H}_9\text{SnClO}_4$: ClO_4 , 38.0. Found: ClO_4 , 38.2. Carbon and hydrogen could not be determined owing to the explosive nature of the compound at high temperatures. Trimethyltin perchlorate melts at 125–127° (sealed tube); it is extremely soluble in methanol and other polar solvents and is very hygroscopic, being converted to a liquid in less than a minute on exposure to moist air. The diammonia adduct was formed when anhydrous ammonia was condensed onto trimethyltin perchlorate and the excess ammonia removed *in vacuo*. *Anal.* Calcd. for $\text{C}_3\text{H}_9\text{SnClO}_4(\text{NH}_3)_2$: C, 12.11; H, 5.01; N, 9.42. Found: C, 12.30; H, 4.87; N, 9.48. This ammonia adduct has low solubility in organic solvents and is stable in air.

Trimethyltin Nitrate.—Trimethyltin bromide (3.166 g., 13.00 mmoles) and anhydrous silver nitrate (2.213 g., 13.02 mmoles) were allowed to react (with shaking on account of the low solubility of silver nitrate) in dry methanol; the silver bromide (2.434 g., 12.96 mmoles) was filtered off and the methanol removed *in vacuo*, to give a white solid. This solid was purified by sublimation at 100° *in vacuo* and gave a white, crystalline sublimate. *Anal.* Calcd. for $\text{C}_3\text{H}_9\text{SnNO}_3$: C, 15.59; H, 3.99; NO_3 , 27.46. Found: C, 16.12; H, 4.33; NO_3 , 27.50. Trimethyltin nitrate melted at 127–128° in a sealed tube and was unaffected by exposure to moist air. It is very soluble in polar solvents such as methanol but has low solubility in non-polar organic solvents. The diammonia adduct was prepared by reaction of the nitrate with anhydrous ammonia as described above. *Anal.* Calcd. for $\text{C}_3\text{H}_{15}\text{N}_3\text{O}_3\text{Sn}$: C, 13.89; H, 5.79; NO_3 , 23.93. Found: C, 14.03; H, 5.58; NO_3 , 24.60.

Discussion

The only compound closely related to trimethyltin perchlorate and trimethyltin nitrate that previously

(1) O. Okawara, D. E. Webster, and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 3287 (1960).

(2) I. R. Beattie and T. Gilson, *J. Chem. Soc.*, 2585 (1961).

(3) G. J. M. Van Der Kerk, J. G. A. Luijten, and M. J. Janssen, *Chimia*, **16**, 10 (1962).

(4) H. Kriegsmann, H. Hoffmann, and S. Pischtschan, *Z. anorg. allgem. Chem.*, **315**, 283 (1962).

(5) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

(6) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *ibid.*, 4222 (1957).

(7) C. C. Addison and B. M. Gatehouse, *ibid.*, 613 (1960).

TABLE I
 INFRARED FREQUENCIES AND ASSIGNMENTS^a

$(\text{CH}_3)_3\text{SnClO}_4$		$(\text{CH}_3)_3\text{SnClO}_4 \cdot 2\text{NH}_3$	
3000 (w) } 2910 (w) }	C-H stretch	3350 (s) } 3260 (s) }	N-H stretch
1405 (m)	Asymm. deform. CH_3	3200 (w)	
1212 (s) } 1192 (s) }	ClO_2^* asymm. stretch or symm. deform. CH_3	2990 (w) } 2900 (w) }	C-H stretch
1112 (s)	ClO_2 asymm. stretch	1610 (m)	Asymm. deform. NH_3
1078 (w, sh)		1425 (m)	Asymm. deform. CH_3
998 (s, br)	ClO_2 symm. stretch	1240 (s)	Symm. deform. of
908 (s)	ClO_2^* symm. stretch	1222 (s)	NH_3 and CH_3
780 (s)	CH_3 rocking	1207 (s)	
625 (m)	ClO_2 symm. bend	1075-1100 (s, br)	ClO_4^- asymm. stretch
606 (m)	Rocking ClO_4	935 (w)	ClO_4^- symm. stretch
552 (m)	Sn-C asymm. stretch	792 (s)	CH_3 rocking
468 (m)	Rocking ClO_4		NH_3 rocking or ClO_4^-
450 (w)	ClO_2^* symm. bend	625 (s)	asymm. bend
		551 (m)	Sn-C asymm. stretch
		~490 (w, sh)	Sn-N stretch?
		441 (w)	ClO_4^- symm. bend

^a ClO_2^* denotes vibrations involving the O atoms which interact with Sn.

has been reported⁸ is trimethyltin fluoroborate, which melts around 89° in a sealed tube and sublimes with decomposition at 100° *in vacuo*. This low melting point and general physical behavior were taken as arguments against the ionic structure $(\text{CH}_3)_3\text{Sn}^+\text{BF}_4^-$, and a relationship was suggested to the unstable $(\text{CH}_3)_3\text{SiBF}_4$.⁹

Trimethyltin perchlorate and trimethyltin nitrate have similar properties; both subliming at low temperatures and melting in sealed tubes at 125-127° and 127-128°, respectively. Their thermal stability, however, is greater than that of the fluoroborate. For these compounds also, their physical properties are not entirely consistent with the ionic structures $(\text{CH}_3)_3\text{Sn}^+\text{ClO}_4^-$ and $(\text{CH}_3)_3\text{Sn}^+\text{NO}_3^-$.

Trimethyltin Perchlorate.—The infrared spectrum of anhydrous trimethyltin perchlorate is shown in Fig. 1 and the observed frequencies and their proposed assignments are listed in Table I.

The two weak bands at 3000 and 2910 cm^{-1} are assigned to the C-H stretching of the CH_3 groups, and the medium intensity band at 1405 cm^{-1} to the asymmetric deformation mode of the CH_3 groups, in accordance with previous assignments.^{1,10} The strong absorptions in the 900-1225 cm^{-1} region are associated with the ClO_4 group and will be discussed shortly. The strong broad band at 780 cm^{-1} is characteristic of the Sn- CH_3 group and has been assigned⁹ to the rocking of the CH_3 groups attached to tin. The absorptions at 625, 606, 468, and 450 cm^{-1} will be discussed later.

In the 500-560 cm^{-1} region, only one band at 552 cm^{-1} is observed, although with a Nujol mull of very high concentration an extremely weak band at approximately 515 cm^{-1} also can be detected. The observation of only one infrared active band of any intensity in this region is consistent with a planar $(\text{CH}_3)_3\text{Sn}$ group,

the 552 cm^{-1} band therefore being assigned as the Sn-C asymmetric stretching vibration. The very weak band at 515 cm^{-1} may be due to a forbidden transition, or it may indicate a slight departure from planarity of the $(\text{CH}_3)_3\text{Sn}$ group. A band of similar intensity is observed for trimethyltin fluoride, the crystal structure of which shows the $(\text{CH}_3)_3\text{Sn}$ groups to be not quite planar.¹¹

The simple perchlorate ion of regular tetrahedral structure has nine vibrational degrees of freedom giving four fundamental frequencies. Of these only two will be infrared active, ν_3 (asymm. stretch) and ν_4 (asymm. bend). The former (ν_3) is observed¹² in solid ionic perchlorates as a broad strong band, usually split, in the 1050-1150 cm^{-1} region, while ν_4 is observed at approximately 630 cm^{-1} . The breathing frequency ν_1 , which is theoretically infrared inactive, also usually is observed as a very weak absorption at 930 cm^{-1} . Aqueous solutions of ionic perchlorates give, in their infrared spectra, one band each for ν_3 and ν_4 , and ν_1 is not observed.¹²

The infrared spectrum of anhydrous trimethyltin perchlorate shows considerable structure between 900 and 1225 cm^{-1} , and is very different from that observed for solid ionic perchlorates. However, after brief exposure to moist air, the compound gives a spectrum (Fig. 1) with absorption maxima at 1095 and 940 cm^{-1} , characteristic of ionic perchlorates. Hydrolysis therefore produces the free ClO_4^- ion.

Hathaway and Underhill⁵ have pointed out that as the perchlorate group becomes involved in partial covalent bonding, its symmetry is lowered from T_d to C_{3v} or C_{2v} according to whether one or two of its oxygen atoms are involved in such bonding. The spectra of anhydrous transition metal perchlorates⁵ show strong absorptions at 1270-1245, 1130, and 948-920 cm^{-1} and a weaker one at 1030 cm^{-1} ; the conclusion is drawn that the perchlorate groups are acting as bidentate

(8) A. B. Burg and J. R. Spielman, *J. Am. Chem. Soc.*, **83**, 2667 (1961).

(9) E. C. Evers, W. O. Freitag, W. A. Kriner, A. G. MacDiarmid, and S. Sujishi, *J. Inorg. Nucl. Chem.*, **13**, 239 (1960).

(10) E. R. Lippincott, P. Mercier, and M. C. Tobin, *J. Phys. Chem.*, **57**, 939 (1953).

(11) H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.*, 85 (1963).

(12) S. D. Ross, *Spectrochim. Acta*, **18**, 225 (1962).

ligands and so have C_{2v} symmetry. Although there is a general shift of 30–40 cm^{-1} to lower frequencies, the spectrum of trimethyltin perchlorate in the 900–1225 cm^{-1} region is very similar to those of anhydrous metal perchlorates and is different from the spectra of lower hydrates of the latter compounds in which the ClO_4 group is considered to behave as a monodentate coordinating group.

From a comparison with $\text{Cu}(\text{ClO}_4)_2$, the following assignments are suggested. The broad peak with maxima at 1212 and 1192 cm^{-1} is assigned as ν_8 , the ClO_2^* asymmetric stretching frequency. However it also should be noted that either the 1212 or the 1192 cm^{-1} band also can be assigned as the symmetrical deformation mode of CH_3 . The 1112 cm^{-1} absorption is assigned as the ClO_2 asymmetric stretching frequency ν_6 . The 998 cm^{-1} peak, which has the same intensity as the 1112 cm^{-1} band, is compared with the unexpectedly weak 1030 cm^{-1} band in $\text{Cu}(\text{ClO}_4)_2$ and is assigned as the ClO_2 symmetrical stretching frequency ν_1 . Finally, the 908 cm^{-1} peak, like the 948–920 cm^{-1} peak in $\text{Cu}(\text{ClO}_4)_2$, is assigned as the ClO_2^* symmetrical stretching frequency ν_2 . The spectrum of trimethyltin perchlorate thus is consistent with C_{2v} symmetry for the ClO_4 group.

This is further supported by the peaks observed in the 350–650 cm^{-1} region. Ionic perchlorates show one band (ν_4) at 630 cm^{-1} , which for solid ionic perchlorates may display fine structure.¹² For a bidentate or bridging ClO_4 group, four bands would be expected theoretically in the KBr region. Anhydrous copper perchlorate⁵ shows six peaks so that some splitting must be involved. Trimethyltin perchlorate shows the expected four bands in this region, at 625, 606, 468, and 450 cm^{-1} . By analogy with $\text{Cu}(\text{ClO}_4)_2$, the 625 cm^{-1} peak tentatively is assigned to the ClO_2 symmetrical bending mode ν_3 , the 606 cm^{-1} band to rocking frequency ν_7 , the 468 cm^{-1} peak to rocking frequency ν_9 , and the weak band at 450 cm^{-1} , observed as a shoulder, to the ClO_2^* symmetrical bending frequency ν_4 .

Ross¹² contends that the splittings in the spectra of various perchlorates, described by Hathaway and Underhill in earlier papers,^{13,14} are attributable to crystal field effects rather than to partial covalent bonding. Certainly the splittings of ν_3 and ν_4 , and the appearance of ν_1 in the spectra of solid alkali metal perchlorates,¹² can be attributed to crystal field effects and are consistent with the observed distortion¹⁵ of the ClO_4 group in crystalline potassium perchlorate. However, the later more detailed discussion by Hathaway and Underhill⁵ clearly shows that the splittings of the infrared bands of anhydrous transition metal perchlorates are of a considerably greater order of magnitude than those observed for salts such as KClO_4 . The same can be said for the multiplicity of peaks and the large splittings observed for trimethyltin perchlorate.

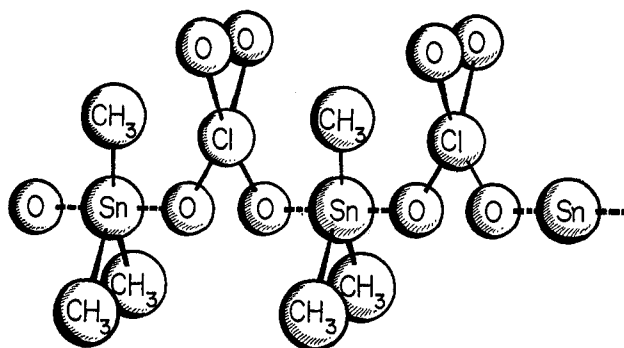


Figure 2.

Moreover, the spectrum of a very concentrated solution of trimethyltin perchlorate in methanol, in which crystal field effects can be ignored, showed absorption bands at 1175, 1115, 1020, and 912 cm^{-1} . The separation and number of these bands, and the frequencies at which they occur, are similar to those found for the solid.

We therefore consider that partial covalent bonding occurs between the $(\text{CH}_3)_3\text{Sn}$ and ClO_4 groups. The $(\text{CH}_3)_3\text{Sn}$ groups are planar and are bridged by ClO_4 groups, probably as shown in Fig. 2. The tin atom will therefore be pentacoordinate, most likely as a trigonal bipyramid as in $(\text{CH}_3)_3\text{SnCl}\cdot\text{py}$ ¹⁶ and in $(\text{CH}_3)_3\text{SnF}$.¹¹

The infrared spectrum of $(\text{CH}_3)_3\text{SnClO}_4\cdot 2\text{NH}_3$ (Fig. 1) shows only one band in the region of 1100 cm^{-1} and there is no maximum (ν_1) at 930 cm^{-1} . Moreover, in the 350–650 cm^{-1} region, the only band that can be associated with the ClO_4 group is observed at 625 cm^{-1} . These absorptions are identical with those observed¹² for solutions of ionic perchlorates and clearly indicate the presence of an undistorted ClO_4^- ion. Only one band is observed in the 500–560 cm^{-1} region, indicating a planar $(\text{CH}_3)_3\text{Sn}$ arrangement. The spectrum therefore is consistent with the formulation $[(\text{CH}_3)_3\text{Sn}(\text{NH}_3)_2]^+\text{ClO}_4^-$, with the tin atom having a trigonal bipyramidal configuration with the two ammonia molecules in the apical position. Similar five-coordination of tin recently has been reported¹⁶ for the compound $(\text{CH}_3)_3\text{SnCl}\cdot\text{py}$.

Trimethyltin Nitrate.—The infrared spectrum of anhydrous trimethyltin nitrate is shown in Fig. 3. Considering first bands arising from the $(\text{CH}_3)_3\text{Sn}$ portion of the molecule, the 3000, 2900, 780, and 557 cm^{-1} bands can be given the same assignments as similar bands in $(\text{CH}_3)_3\text{SnClO}_4$, although it is clear that the 780 cm^{-1} band is overlapped by at least one band at 825 cm^{-1} and possibly another. The band at 520 cm^{-1} is assigned to Sn–C symmetric stretch, this band approaching in intensity the similar band in trimethyltin chloride.¹ Clearly, the $(\text{CH}_3)_3\text{Sn}$ group is not planar.

Anhydrous metal nitrates containing the nitrate ion NO_3^- (D_{3h} symmetry) show absorption at 1390, 1050, 831, and 720 cm^{-1} , while compounds in which the nitrate group is covalently bound through one oxygen

(13) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 653 (1960).(14) B. J. Hathaway and A. E. Underhill, *ibid.*, 3709 (1960).(15) C. D. West, *Z. Krist.*, **91**, 480 (1935).(16) I. R. Beattie, G. P. McQuillan, and R. Hulme, *Chem. Ind. (London)*, 1429 (1962).

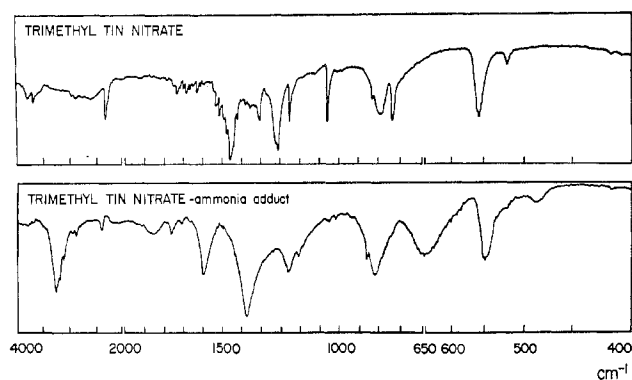


Figure 3.

atom show absorption bands at 1531–1481, 1290–1253, 1034–970, 800–781, 739, and 713 cm^{-1} .

Assignments of these bands have been made both for metal-nitrato complexes,⁶ and for some anhydrous metal nitrates,⁷ but in the present instance, comparison can best be made with the reported spectrum of $\text{Mn}(\text{CO})_5\text{NO}_3$,¹⁷ in which NO_3 must be present as the unidentate nitrato group, $-\text{ONO}_2$, of C_{2v} symmetry.

	ν_4 NO_2 asymm. stretch	ν_1 NO_2 symm. stretch	ν_2 NO stretch	ν_6 $-\text{ONO}_2$ out of plane
$\text{Mn}(\text{CO})_5\text{NO}_3$	1486	1284	1010	805
$(\text{CH}_3)_3\text{SnNO}_3$	1488	1268	1031	780

The $-\text{ONO}_2$ out-of-plane vibration, ν_6 , usually is observed in the 800–781 cm^{-1} region, but is here either overlapped by the intense 780 cm^{-1} band due to CH_3 rocking, or less likely is observed as the 825 cm^{-1} band. The NO_2 symmetric and asymmetric bending vibrations do not seem to be resolved and probably appear as the 727 cm^{-1} band.

It must, however, be pointed out that both a unidentate $-\text{ONO}_2$ group and a bridging $\begin{array}{c} \text{O} \\ | \\ \text{O} > \text{N} - \text{O} \end{array}$ group have essentially the same symmetry and for an unambiguous assignment a comparison with the spectrum of a nitrate containing a bridging NO_3 group is necessary. Basic beryllium nitrate, $\text{Be}_4\text{O}(\text{NO}_3)_6$, is considered¹⁸ to contain such bridging groups, and its infrared spectrum¹⁹ is very different from that of either $\text{Mn}(\text{CO})_5\text{NO}_3$ or $(\text{CH}_3)_3\text{SnNO}_3$, the most noticeable difference being the complete absence of any 1490 cm^{-1} band. This confirms that trimethyltin nitrate contains a unidentate $-\text{ONO}_2$ nitrato group.

(17) C. C. Addison, M. Kilner, and A. Wojcicki, *J. Chem. Soc.*, 4839 (1961).

(18) C. C. Addison and A. Walker, *Proc. Chem. Soc.*, 242 (1961).

(19) C. C. Addison and A. Walker, private communication.

The nitrate also forms a diammonia adduct, $(\text{CH}_3)_3\text{SnNO}_3 \cdot 2\text{NH}_3$, whose infrared spectrum is shown (Fig. 3). The principal absorption frequencies are 3200–3300 (N-H stretch), 3000–2900 (C-N stretch), 1610 (asymm. deform. NH_3), 1360 (NO_2 stretch), 1210 (CH_3 or NH_3 symm. deform.), 827 (NO_3^- out-of-plane), 785 (CH_3 rocking), 720 (shoulder; NO_2 bending), 650 (NH_3 rocking), 552 (Sn-C asymm. stretch), and 475 cm^{-1} (Sn-N stretch?).

Clearly, the observed frequencies of 1360, 827, and 720 cm^{-1} , together with the weak band at 1035 cm^{-1} , are those associated with a free NO_3^- ion and are very different from those observed for the NO_3 group in the anhydrous nitrate. The compound therefore is best described as $(\text{CH}_3)_3\text{Sn}(\text{NH}_3)_2^+\text{NO}_3^-$. Only a very weak shoulder is found at 520 cm^{-1} , in comparison with an intense band at 552 cm^{-1} . The $(\text{CH}_3)_3\text{Sn}$ group therefore presumably is essentially planar. The bands at 3200–3300, 1610, and possibly 1210 and 650 cm^{-1} are those associated with coordinated NH_3 groups, although some of these bands tend to differ in shape from those reported²⁰ for other amines. Thus, the 1600 cm^{-1} band usually is broad, but in this compound and also in $(\text{CH}_3)_3\text{SnClO}_4 \cdot 2\text{NH}_3$ this band is very sharp.

It is interesting that both the nitrate and perchlorate adducts show weak bands at approximately 500 cm^{-1} , in good agreement with previous assignments²⁰ for metal-nitrogen stretching vibrations in amines.

That the nitrate should maintain an essentially tetrahedral structure around the tin atom, while the perchlorate contains five-coordinate tin in a chain-like structure, is perhaps not surprising. The latter structure more nearly approaches the ionic arrangement that might be expected for a perchlorate; the occurrence of partial covalent bonding even with a perchlorate group seems to indicate an inherent instability of the planar $(\text{CH}_3)_3\text{Sn}^+$ cation. This is supported by the structure of trimethyltin fluoride,¹¹ in which some covalent interaction also occurs. We are now investigating compounds such as $(\text{CH}_3)_3\text{SnBF}_4$ and $(\text{CH}_3)_3\text{SnPF}_6$ and our preliminary results again indicate that there is little tendency for the existence of the free planar $(\text{CH}_3)_3\text{Sn}^+$ ion.

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(20) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 3108 (1956).