We are now engaged in further study of analogous systems.

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Contribution from the Department of Chemistry,
University of British Columbia, Vancouver, British Columbia, Canada

Reactions of Organotin Compounds. V. Studies of Additional Tri- and Diorganotin Derivatives[1]

By H. C. CLARK and R. G. GOEL

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In a further study of five-coordination of tin in compounds of the type R_3SnX, triphenyltin perchlorate and nitrate have been studied spectroscopically. It is concluded that their structures are probably identical with those of their methyl analogs. Contrary to previous reports, triphenyltin nitrate was found to be stable under anhydrous conditions. Studies of trimethyltin sulfate and chromate are reported. The infrared spectrum of dimethyltin chromate provides strong evidence for coordination by the chromate group and further emphasizes the remarkably strong interaction that is consistently observed between the R_3Sn^+ and R_2Sn^{2+} ions and all anions.

Introduction

Five-coordination of tin has been proposed for a number of trialkyltin derivatives, including those of very strong acids, *e.g.*, trimethyltin perchlorate,[2] trimethyltin tetrafluoroborate,[3,4] and trimethyltin hexafluoroantimonate.[4] In at least one instance,[5] chloro(trimethyl)pyridinetin(IV), a full X-ray structure determination and infrared spectroscopic studies conclusively establish both the planarity of the trimethyltin group and the five-coordination of tin. For the derivatives of strong acids, much of the evidence has been obtained by infrared spectroscopy whereby "coordination" by, say, perchlorate to trimethyltin has been deduced from the observation that the perchlorate has C_{2v} (or lower) symmetry, in accord with behavior as a bidentate or bridging group. Such a lowering of symmetry in the solid state could be attributed to coordination, a conclusion reached from similar evidence for some transition metal complexes, *e.g.*, $Cu(ClO_4)_2$,[6] and 3,5-lutidine complexes of nickel(II) perchlorate and tetrafluoroborate.[7] Alternatively, crystal field effects (*i.e.*, low site symmetry) could produce such spectroscopic effects, and this possibility will be considered more fully later in this paper. If coordination of X to R_3Sn occurs, three questions are raised: (i) Does the nature of R have any influence on the interaction between R_3Sn and X? (ii) What is the nature of the interaction? (iii) Do similar effects occur between X and R_2Sn in the derivatives R_2SnX_2? In attempting to distinguish between coordination and crystal field effects and to answer these questions we have (a) examined two triphenyltin compounds, since on analogy with the triphenylcarbonium ion the triphenyltin cation may well possess greater stability than trialkyltin cations, (b) attempted the preparation of triorganotin derivatives of some transition metal oxyanions, and (c) studied dimethyltin chromate.

Experimental

Compounds were prepared and handled by conventional vacuum techniques or under a nitrogen atmosphere in a drybox. Solvents were of either Spectro grade or Mallinckrodt A.R. grade. Infrared spectra were determined using a Perkin-Elmer Model 21 double-beam recording spectrophotometer (NaCl optics) and a Perkin-Elmer Model 421 spectrophotometer. Samples were prepared in the drybox as mulls in Nujol, hexachlorobutadiene, or halocarbon oil.

Triphenyltin Perchlorate.—Anhydrous silver perchlorate (1.092 g.) and triphenyltin chloride (2.030 g.) were shaken in anhydrous ether for 3 days. Silver chloride was filtered off, and the solvent was removed under vacuum at room temperature, to leave a white solid. *Anal.* Calcd. for $C_{18}H_{15}SnClO_4$: C, 48.2; H, 3.34. Found: C, 48.9; H, 3.38. Triphenyltin perchlorate is very soluble in both methanol and ether and is hydrolyzed in moist air, becoming liquid after approximately 1 day.

Anhydrous ammonia (dried over sodium metal) was condensed onto a sample of the solid perchlorate, and onto a solution of the perchlorate in anhydrous methanol. Both mixtures were kept at −70° for 24 hr., after which the excess ammonia and solvent were removed *in vacuo*, to leave white solids. Analytical results were not reproducible but were always of the same order, a typical result being as follows. *Anal.* Calcd. for $C_{18}H_{21}SnClO_4N_2$: C, 44.75; H, 4.35; N, 5.79. Calcd. for $C_{18}H_{18}SnClO_4N$: C, 46.35; H, 3.86; N, 3.00. Found: C, 44.63; H, 4.63; N, 3.99. X-Ray powder photographs showed that all mixtures contained ammonium perchlorate.

Triphenyltin Nitrate.—(a) Silver nitrate (1.00 g.) and tri-

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(1) Part IV: *J. Organometal. Chem.*, in press.

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TABLE I

ANION INFRARED ABSORPTION BANDS (CM.$^{-1}$) IN TRIPHENYLTIN PERCHLORATE AND NITRATE[a]

$(C_6H_5)_3SnClO_4$ (anhydrous)		$(C_6H_5)_3SnNO_3$ (anhydrous)		$(C_6H_5)_3SnNO_3$ (wet)	
1200 vs	$ClO_2{}^b$ asym. str.	1515 s	NO_2 asym. str. ν_4		
1112 vs	ClO_2 asym. str.	1508 s		1393 vs	NO_2 asym. str. ν_3
985 vs	ClO_2 sym. str.	1492s			
905 s	$ClO_2{}^b$ sym. str.	1288 s	NO_2 sym. str. ν_1	826 m	$NO_3{}^-$ out-of-plane bend ν_2
625 m	ClO_2 sym. bend	1271 s			
610 sh	ClO_4 rocking	1257 s			
		978 m	NO str. ν_2		
604 sh					
455 sh	ClO_4 rocking, $ClO_2{}^b$ sym. bend and Sn–phenyl (?)	798 m	$-ONO_2$ out-of-plane bend ν_6		
449 s					
439 sh					

[a] vs, very strong; s, strong; m, medium; sh, shoulder. [b] Denotes the two bridging oxygen atoms.

phenyltin chloride (2.26 g.) were shaken in dry acetone for 3 days. The precipitated silver chloride was filtered off and the dry acetone removed under vacuum. The same reaction was also performed, more rapidly and without shaking, in dry methanol owing to the greater solubility of silver nitrate in this solvent. The product was a white solid. *Anal.* Calcd. for $C_{18}H_{15}SnNO_3$: C, 52.42; H, 3.67; N, 3.39. Found: C, 51.90; H, 3.70; N, 3.32.

(b) Triphenyltin nitrate was also prepared by mixing solutions of triphenyltin chloride (3.855 g.) in 50 ml. of acetone and silver nitrate (1.698 g.) in 5 ml. of water. The precipitated silver chloride was filtered off, and the solvent was removed under vacuum. The product and the removed solvent were both yellow in color, suggesting some decomposition. *Anal.* Calcd. for $C_{18}H_{15}SnNO_3$: C, 52.42; H, 3.67; N, 3.39. Found: C, 53.53; H, 4.40; N, 3.23.

Stability of Triphenyltin Nitrate.—Anhydrous triphenyltin nitrate was found to be stable at room temperature in the drybox for more than 2 months. After this time, there were no changes in appearance, nor in the infrared spectrum. However, exposure of the anhydrous compound to moist air caused marked changes in the infrared spectrum. Some changes also occurred when a sample of the anhydrous compound was heated to 150° under vacuum for 1.5 hr. A sample of the nitrate prepared from wet acetone was heated in *o*-dichlorobenzene as described by Shapiro and Becker,[8] and the infrared spectra of the residue and of the yellow distillate were recorded.

Reaction with Ammonia.—Anhydrous triphenyltin nitrate, as the solid or in dry methanol solution, was allowed to react with excess dry ammonia under the same conditions as described earlier for the perchlorate. The products were white solids which gave nonreproducible analytical results, the following being typical. *Anal.* Calcd. for $C_{18}H_{21}SnN_3O_3$: C, 48.44; H, 4.75; N, 9.42. Calcd. for $C_{18}H_{18}SnN_2O_3$: C, 50.35; H, 4.23; N, 6.53. Found: C, 50.31; H, 4.76; N, 5.88. X-Ray powder photographs and the infrared spectra showed these to be mixtures, since all the lines of ammonium nitrate were observed.

Trimethyltin Sulfate.—Trimethyltin bromide (1.220 g.) and silver sulfate (0.781 g.) were shaken in 50 ml. of dry methanol. The silver bromide was filtered off (0.945 g., calcd. 0.941 g.), and on removal of the methanol under vacuum at 25°, white crystals of $[(CH_3)_3Sn]_2SO_4(CH_3OH)_2$ were obtained. *Anal.* Calcd.: C, 19.68; H, 4.13; SO_4, 19.70. Found: C, 19.00; H, 4.59; SO_4, 20.48. This product is readily dissolved in water and methanol and is rapidly hydrolyzed on exposure to air. When heated under vacuum at 100° for 4 hr., the methanol was removed, to give white $[(CH_3)_3Sn]_2SO_4$. *Anal.* Calcd.: C, 17.01; H, 4.25. Found: C, 17.55; H, 4.46. This product was also rapidly hydrolyzed on exposure to air, as shown by changes in its infrared spectrum.

Trimethyltin Chromate.—Trimethyltin bromide (2.793 g.) and silver chromate (1.901 g.) were mixed in 50 ml. of dry methanol. Silver bromide (2.142 g., calcd. 2.152 g.) was immediately precipitated and filtered off. The methanol was quickly removed under vacuum at 25° to give yellow crystals of $[(CH_3)_3Sn]_2CrO_4$. *Anal.* Calcd.: C, 16.24; H, 4.06; CrO_4, 26.17. Found: C, 16.08; H, 4.00; CrO_4, 25.46. Trimethyltin chromate is soluble in water and methanol, but decomposes slowly in solution as shown by the gradual darkening of color; it is only slightly soluble in acetone and insoluble in ether. Unlike trimethyltin sulfate, it is not hydrolyzed in moist air; samples exposed to air for 3 days showed no change spectroscopically.

Dimethyltin Chromate.—Dimethyltin chloride (1.800 g.) and silver chromate (2.718 g.) were shaken in 50 ml. of dry acetone for 24 hr. A yellow mixture of silver chloride and dimethyltin chromate was obtained from preparations carried out in dry acetone or acetonitrile, and, in each case, an X-ray powder photograph showed the presence of silver chloride and the absence of dimethyltin dichloride. On addition of the mixture to water acidified with acetic acid, there was no precipitation, only the settling of the previously-formed insoluble silver chloride in quantitative amounts. From the filtrate, the quantitative weight of barium chromate was precipitated, confirming that there had been no reduction of the chromium. A preparation was attempted in dry methanol, but although silver chloride could be filtered off, the slightly soluble dimethyltin chromate reacted with the methanol, as shown by a fairly rapid darkening in color, so that the pure product could not be isolated.

Discussion

We have previously shown[2] that the infrared spectrum of trimethyltin perchlorate is in accord with the perchlorate group having C_{2v} symmetry and the trimethyltin group being planar. The most probable, generalized structure is a polymeric chain structure in which ClO_4 groups act symmetrically as bridges between $(CH_3)_3Sn$ groups, making the tin atoms five-coordinate, although other structures can also be suggested (*e.g.*, an unsymmetrical bridged structure as in trimethyltin fluoride[9] or some type of cyclic structure).

The observed infrared absorption bands of the perchlorate group in triphenyltin perchlorate are listed with their relative intensities and probable assignments in Table I. The bands arising from ClO_4 are identical with those observed for trimethyltin perchlorate, again clearly indicating that the ClO_4 group cannot have symmetry higher than C_{2v}. With respect to the triphenyltin group, there are no apparent differences between the spectra of triphenyltin chloride,[10,11] triphenyltin azide,[12] and triphenyltin perchlorate.

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Triphenyltin chloride is considered[11] to be nonassociated so that the triphenyltin groups should be nonplanar, while triphenyltin azide is reported[13] to be composed of planar triphenyltin groups bridged by azide groups. No conclusions can therefore be reached concerning the geometry of the triphenyltin group in the perchlorate on the basis of its infrared spectrum. Moreover, there is considerable disagreement concerning the frequencies at which absorption due to the symmetric and asymmetric stretching vibrations of the phenyl–tin bonds should be observed. Griffiths and Derwish[10] have assigned a weak band at 1164 cm.$^{-1}$ in the spectrum of triphenyltin chloride to the phenyl–tin asymmetric stretching mode, but Kriegsman and Geissler[11] have assigned this mode to the band observed at 450 cm.$^{-1}$. The latter is, in our opinion, probably correct, but without at least one definitive structure determination of a triphenyltin compound it is clearly not possible to describe the configuration of the triphenyltin group in triphenyltin perchlorate with any certainty. In view of the almost identical spectra of the ClO_4 group in trimethyltin and triphenyltin perchlorates it seems reasonable to suggest a similar structural function for the ClO_4 group in the two compounds.

The two spectra also change similarly when the perchlorates are exposed to moist air.[2] For triphenyltin perchlorate, the four intense bands at 905, 985, 1112, and 1200 cm.$^{-1}$ are replaced by an intense broad band in the 1075–1150 cm.$^{-1}$ region and a weak band at 940 cm.$^{-1}$. These are characteristic of the free ClO_4^- ion,[14] which has been formed by the hydrolysis of the anhydrous perchlorate.

The infrared absorption bands of the NO_3 group in triphenyltin nitrate are listed with their intensities and assignments, for both preparations of the compound, in Table I. The convention described by Addison and Gatehouse[15] is used in numbering the vibrations of the NO_3 group. The anhydrous nitrate clearly contains an NO_3 group of C_{2v} or lower symmetry,[2,16] and it is interesting that both ν_4 (NO_2 asymmetric stretch) and ν_1 (NO_2 symmetric stretch) show a secondary splitting into triplets. This effect, at present unexplained, is also seen[17] in the complex $Co[(CH_3)_3PO]_2(NO_3)_2$, which apparently contains a bidentate nitrate group. On the basis of infrared spectra alone, it is as yet not possible to distinguish unambiguously between bridging, bidentate, or monodentate NO_3 groups, but certainly in anhydrous triphenyltin nitrate the NO_3^- ion is *not* present. The absorptions of the triphenyltin group are the same as those of triphenyltin perchlorate and other triphenyltin compounds, and again no conclusions can be reached as to the shape of the $(C_6H_5)_3Sn$ group.

In contrast, triphenyltin nitrate prepared from wet acetone gives the infrared peaks of the free NO_3^- ion,[16] and the same spectrum is also observed when anhydrous nitrate is exposed to moist air, the changes in the spectrum being complete after an exposure of 24 hr.

Shapiro and Becker[8] have reported that triphenyltin nitrate, prepared in wet acetone, decomposed spontaneously at 25° to give nitrobenzene and diphenyltin oxide, and at higher temperatures to give nitrobenzene, benzene, and diphenyltin oxide. Our own results show that there is clearly a constitutional difference between the anhydrous and wet nitrates and that the wet product is probably at least partially hydrated. The anhydrous nitrate is appreciably stable as shown by (a) the lack of any spectroscopic changes in a sample stored for at least 2 months at 25° and (b) the minor spectroscopic changes observed for a sample which had been heated at 150° for 1.5 hr. Even the wet nitrate did not change in appearance or spectroscopically over periods of several days, although when heated with *o*-dichlorobenzene as described by Shapiro and Becker, decomposition was complete. We conclude that pure triphenyltin nitrate is stable under anhydrous conditions and that the instability observed by Shapiro and Becker is associated to some degree with the presence of moisture and possibly of some catalytic impurities.

Attempts to obtain by reaction with anhydrous ammonia the adducts $(C_6H_5)_3Sn(NH_3)_2X$ (where $X = ClO_4$ or NO_3) were not successful. The reaction products were mixtures of the corresponding ammonium salt NH_4X and bis(triphenyltin) oxide. The latter can be easily identified by means of the characteristic infrared band at 774 cm.$^{-1}$ which has been assigned[18] as a vibration of the Sn–O–Sn group. The reactions with ammonia must proceed as follows

$$(C_6H_5)_3SnX + NH_3 \longrightarrow [(C_6H_5)_3SnX\cdot NH_3] \xrightarrow{H_2O} [(C_6H_5)_3Sn]_2O + 2NH_4X$$

and are consistent with a report by Kupchik and Lanigan,[19] who found the products of reaction between triphenyltin bromide and ammonia to be bis(triphenyltin) oxide and ammonium bromide. It is clear that ammonia derivatives of triphenyltin compounds have a very low hydrolytic stability, for either kinetic or thermodynamic reactions, and that in the present case hydrolysis occurred even under carefully controlled conditions.

Our results thus indicate that for the compounds R_3SnClO_4 and R_3SnNO_3 the structures are not significantly affected by changing R from methyl to phenyl, suggesting that the nature of R has little if any influence on the interaction between R_3Sn and X.

Attempts to prepare trimethyltin permanganate, $(CH_3)_3SnMnO_4$, were unsuccessful. This compound was sought since a study of its infrared spectrum, and also its visible–ultraviolet absorption spectrum, might provide information on the interaction between $(CH_3)_3$-

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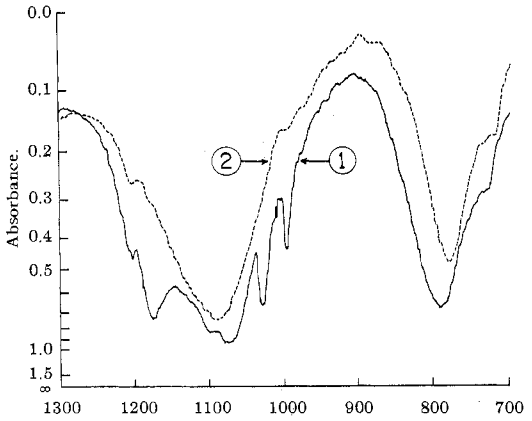

Figure 1.—The infrared spectra of bis(trimethyltin) sulfate methanol adduct (curve 1), and bis(trimethyltin) sulfate (curve 2), in Nujol mulls.

Sn$^+$ and MnO_4^-. Trimethyltin chromate, $[(CH_3)_3Sn]_2CrO_4$, however, could be readily synthesized, but in this compound, formally at least, a doubly-charged anion, CrO_4^{2-}, is present so that the stoichiometry is quite different from that involving only singly-charged anionic groups such as ClO_4^-. For this reason, to provide a comparison, trimethyltin sulfate was also prepared. The first product of the preparation in methanol was the methanol adduct, $[(CH_3)_3Sn]_2SO_4 \cdot 2CH_3OH$, from which the methanol was completely removed by heating under vacuum at 100° for 4 hr. Parts of the infrared spectra of the adduct and the nonsolvated product are shown in Figure 1. For both products, the trimethyltin group shows absorption at 2900–3000 (C–H stretch), 780–785 (Sn–CH_3 rocking), and 552 cm.$^{-1}$ (Sn–C asymmetric stretch), in accord with a planar geometry. It is noteworthy that in these and all other similar cases, the Sn–C asymmetric stretching vibration is observed at frequencies higher than 550 cm.$^{-1}$. The shift to higher frequencies from 540–545 cm.$^{-1}$, observed[20,21] for tetrahedral trimethyltin compounds, is consistent with a change to a planar trimethyltin group.[22] In the adduct, bands due to the SO_4 group are observed at 1165 (s), 1095 (s, sh), 1065 (s), 1021 (m), 989 (m), 630 (s), 595 (m), 558 (sh), and 447 (br, m) cm.$^{-1}$, while in the nonsolvated sulfate, only the broad ν_3 vibration at 1090 cm.$^{-1}$ and ν_4 at 630 cm.$^{-1}$ are observed, as expected, for a tetrahedral SO_4 group of T_d symmetry. The observed splittings of the sulfate bands in the methanol adduct can be explained in a number of ways, one of which would involve coordination[23] of SO_4 of C_{2v} symmetry to planar trimethyltin groups. The methanol molecules are probably also coordinated, since the OH absorption is observed as a broad band at 3100–3150 cm.$^{-1}$, lowered from the 3350 cm.$^{-1}$ band observed for methanol itself. The spectrum of the nonsolvated sulfate can be interpreted in terms of ions, planar $(CH_3)_3Sn^+$ and SO_4^{2-}, or equally well in terms of a coordinated model where *every* oxygen on *each* SO_4 group is coordinated to a tin atom, preserving the T_d symmetry of SO_4. As a result of the molecular stoichiometry, the infrared spectrum does not provide any differentiation between these two models.

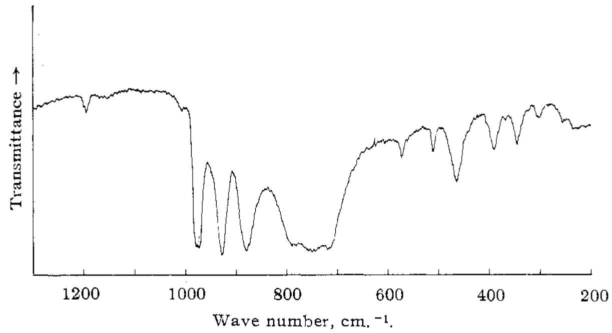

Figure 2.—The infrared spectrum of the dimethyltin chromate–silver chloride mixture, in a Nujol mull.

This is also true for trimethyltin chromate, $[(CH_3)_3Sn]_2CrO_4$. The main features of its infrared spectrum are the ν_3 mode of chromate[24] at 885 cm.$^{-1}$, the Sn–CH_3 rock at 750 cm.$^{-1}$, and the Sn–C asymmetric stretch at 554 cm.$^{-1}$. The weak doublet (ν_4) usually observed at 368 cm.$^{-1}$ for CrO_4^{2-} was not observed even in highly concentrated Nujol mulls. However, the CrO_4 group appears to have T_d symmetry, and the $(CH_3)_3Sn$ group to be planar. Both features are consistent with a structure in which all four oxygen atoms on CrO_4 are involved in coordination, and again the infrared evidence does not distinguish between an ionic and a coordinated structure.

To explore further the possibility of coordination by CrO_4^{2-} to tin, we have studied spectroscopically $(CH_3)_2SnCrO_4$. The infrared spectrum is shown in Figure 2. Dimethyltin chromate shows a remarkably large splitting of ν_3 as well as other changes in its infrared spectrum that seem explicable only in terms of a coordinated CrO_4 group. The ν_3 frequency observed at 884 cm.$^{-1}$ for CrO_4^- ions is resolved into three components of equal intensity at 880, 928, and 975 cm.$^{-1}$, while ν_1, observed only as a weak band at 845 cm.$^{-1}$ for CrO_4^- ions, is apparently one of the components giving rise to strong absorption in the 720–800 cm.$^{-1}$ region; another component is the Sn–CH_3 rocking frequency. At lower frequencies, four bands can clearly be assigned to CrO_4, namely at 465, 390, 348, and 305 cm.$^{-1}$, although an Sn–O vibration may also cause absorption in this region. Certainly the chromate spectrum can only be interpreted in terms of C_{2v} symmetry. The dimethyltin group shows, apart from C–H stretching (2900–3000 cm.$^{-1}$), Sn–CH_3 rocking, and CH_3 deformation (1202 and 1400 cm.$^{-1}$) frequencies, two bands of medium intensity at 512 and 573 cm.$^{-1}$, which are assigned to Sn–C symmetric and asymmetric stretching vibrations. Since the spec-

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trum was obtained for a mixture of silver chloride and dimethyltin chromate, the possibility must be considered that some of these bands are due to unreacted $(CH_3)_2SnCl_2$. This can be rejected, however, (a) by the analytical and X-ray results for the mixture (the latter shows no lines of $(CH_3)_2SnCl_2$ in the powder photograph), (b) by the fact that the spectrum of the mixture does not show the very intense Sn–Cl stretching vibrations[25,26] in the 308, 338 cm.$^{-1}$ regions, and (c) by the fact that the observed Sn–C stretching vibrations differ slightly from those of $(CH_3)_2SnCl_2$ (515 and 567 cm.$^{-1}$). The spectrum is therefore due *only* to dimethyltin chromate, which must contain CrO_4 groups of C_{2v} symmetry, or possibly lower, and nonlinear $(CH_3)_2Sn$ groups. A coordinated structure is therefore proposed, similar to that of trimethyltin perchlorate,[2] the CrO_4 groups acting as bridging groups between $(CH_3)_2Sn$ units, the tin atoms having a tetrahedral environment. A monomeric structure containing a bidentate chromate group is also possible.

The ultraviolet and visible diffuse reflectance spectra of powdered samples of trimethyltin chromate and dimethyltin chromate were examined, since coordination by CrO_4 might cause some changes from the spectrum of CrO_4^{2-}. However, trimethyltin chromate showed absorption maxima at 310 and 420 mμ, and dimethyltin chromate at 280 and 380 mμ, showing virtually no changes from the maxima observed[27] at 275 and 375 mμ for powdered potassium chromate. This is in agreement with the spectrum[28] of the complex $[Co(NH_3)_5CrO_4]^+$, which is very similar to that of CrO_4^{2-}, showing that coordination of CrO_4^{2-} through an oxygen atom has almost no effect on the charge-transfer spectrum.

The possibility exists that many of the above infrared spectroscopic effects (*i.e.*, splitting of bands, etc.) are due to crystal state effects and not to coordination, but in our opinion this can be rejected for the present study and our earlier studies of R_3SnX derivatives,[2,4] on the following grounds.

(1) The reported[29] crystal structure of trimethyltin fluoride, containing a nonlinear, nonsymmetrical Sn–F---Sn bridge, cannot be interpreted as purely ionic and strongly suggests that some other type of coordinative interaction is involved, making the Sn atom five-coordinate.

(2) Similar infrared splittings have been observed[30] for trimethyltin perchlorate in methanol solution, where crystal state effects are completely absent. Moreover, the fact that in solution the symmetry of the perchlorate group is significantly lowered must indicate the presence of strong directional forces. These results can, of course, be interpreted in terms of either $Sn-OClO_3$ bond formation *or*, alternatively, of association of solvated $(CH_3)_3Sn^+$ and ClO_4^- ions. This is, however, the first observation of such interaction with a perchlorate group *in solution*, despite recent investigations,[31] and stresses the strength of the interaction arising from the $(CH_3)_3Sn$ group.

(3) Recent studies[32] have been made of a large number of chromates containing a wide variety of cations, in an attempt to correlate low site symmetries in the crystal state with observed splittings of the chromate infrared bands. Not even in ammonium chromate, where hydrogen bonding is known to occur, were such large and well-defined splittings of ν_3 observed, and, most importantly, only minor effects were observed in the 200–500 cm.$^{-1}$ region, in contrast to the significant splittings seen for dimethyltin chromate. The entire order of the infrared effects observed for dimethyltin chromate is quite different from those attributable to crystal state effects.

(4) In dimethyltin dinitrate, similar infrared results are consistent with ultraviolet spectroscopic studies[33] in suggesting covalent bonding of the nitrate group, although this does not, of course, justify any extrapolation to other anionic groups. Other chemical evidence also reveals this strong interaction exerted by R_2Sn or R_3Sn on anions (*e.g.*, decomposition[4] of $(CH_3)_3SnPF_6$ and the complete decomposition[34] of $(CH_3)_2SnSiF_6$ to $(CH_3)_2SnF_2$ and SiF_4). Similar evidence has been obtained[34] for the corresponding R_3SbX_2 compounds.

We must stress that our main contention is that an intense interaction is exerted by R_2Sn or R_3Sn on any anion. We believe that this interaction is of a coordinative type, in which case the d orbitals of the tin atoms may well be involved, as suggested by other workers.[35] Alternatively, very strong polarization by the organotin cations may produce these spectroscopic effects, although there is no obvious reason why these simple cations of low charge density should be more strongly polarizing than any other known cation. Unfortunately, there is no obvious experimental method which will distinguish unambiguously between models based on such qualitative terms as "polarization," "coordination," and "covalent bond." Clearly, however, none of these compounds contains free R_3Sn^+ or R_2Sn^{2+} cations. In later papers we will describe related studies of other R_2SnX_2 compounds, and of R_3SbX_2 compounds.

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