Raman, Infrared, and Nuclear Magnetic Resonance Spectroscopic Studies on Aqueous Solutions of Dimethyltin(IV) Compounds: Structure and Bonding of the Aquodimethyltin Ion[1]

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The Raman and infrared spectra of aqueous solutions of dimethyltin perchlorate and nitrate have been determined, and a complete vibrational assignment has been made on the basis of a linear C–Sn–C skeleton with an effective point group of D_{3d}. No lines attributable to tin–oxygen stretching frequencies were observed, and it is concluded that probably four water molecules are coordinated about the cation in the equatorial plane by highly polar bonds. It is suggested that under such conditions maximization of the s-character in the metal orbitals used to bind the alkyl groups will be the rule for organometallic cations in polar solvents. The Raman spectra of solutions containing excess chloride ion show lines in addition to those observed for the free cation. Since this spectrum is very similar to that found for pure, liquid $(CH_3)_2SnCl_2$, and the lines can be assigned on the basis of C_{2v} symmetry, strong complexing by chloride ion with the formation of $[(CH_3)_2SnCl]^+$ is indicated. It is probable that the C–Sn–C angle is appreciably less than 180° in this complex. It is also concluded that the structure of the monohydroxo complex $[(CH_3)_2SnOH]^+$ formed in aqueous solution is similar. The bonding in these and similar complexes is discussed in terms of the tin-117 and tin-119 proton coupling constants as determined from proton resonance spectra of the solutions.

Introduction

The dissolution of dialkyltin dihalides R_2SnX_2 in water proceeds with almost complete aquation to the dimethyltin(IV) ion, and these compounds in dilute solution behave as bi-univalent electrolytes.[3] It is well known on the basis of electron diffraction measurements[4] that the dihalides are tetrahedral in the gaseous state. Studies on the infrared spectra indicate that the tetrahedral coordination of the tin atom is still maintained in the liquid and solid halides.[5] It has been assumed generally that the tetrahedral coordination is maintained in the aquo ions, so that dissolution would proceed with the substitution of the two halogens by water molecules.[6,7] The aquo ions would, therefore, be considered as $[R_2Sn(OH_2)_2]^{+2}$. The only real experimental evidence for this type of structure involves the interpretation of an experiment performed many years ago by Pope and Peachy.[8] Unfortunately, attempts to repeat the experiments in the intervening years have not proved successful.[9]

Studies on the hydrolysis of the dimethyltin cation in a perchlorate medium indicated that no polycondensed species with more than about four tin atoms existed at appreciable concentrations in these solutions, and this tended to indicate less than six coordinations for the tin atom.[10] In particular the unusual stability of the binuclear complex $[(CH_3)_2Sn(OH)_2Sn(CH_3)_2]^{+2}$ and at higher pH the mononuclear $(CH_3)_2Sn(OH)_2$ was in accord with tetrahedral coordination about the tin atom.

Some time ago, it was noted that the tin–proton coupling constants obtained with solutions of dimethyltin dichloride were very dependent upon the particular solvent employed.[11] Since the ^{119}Sn resonance was being studied in these early experiments, the coupling constants were not obtained with any great precision. Later, it was suggested on the basis of proton n.m.r. measurements that a linear relation existed between the $^{117}Sn–CH_3$ or $^{119}Sn–CH_3$ coupling constants and the per cent s-character in the tin orbitals directed to the methyl groups.[12,13] By assuming 25% s-character in the tin orbitals in $Sn(CH_3)_4$, Holmes and Kaesz pointed out that extensive rehybridization apparently accompanied the aquation of dimethyltin dichloride with nearly 50% s-character in the orbitals directed to carbon. The data for aqueous solutions of $(CH_3)_3SnCl$ also indicated extensive rehybridization with slightly over 30% s-character in the tin orbitals to carbon, and recently many solid compounds have been prepared in which planar SnC_3 or almost planar skeletons apparently occur, e.g., $(CH_3)_3Sn(NH_3)_2X$ $(X = ClO_4^-, NO_3^-)$,[14] $(CH_3)_3SnClO_4$,[15] $(CH_3)_3SnF^{16}$ (slight deviations from planarity), $(CH_3)_3SnBF_4$,[17] $(CH_3)_3SnY$ $(Y = AsF_6^-$ and $SbF_6)^-$,[18] and the trimethyltin carboxylates.[19,20]

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(17) B. J. Hathaway and D. E. Webster, *ibid.*, 14 (1963).

(18) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 1020 (1963).

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

(20) G. J. M. van der Kerk, J. G. A. Luijten, and M. J. Janssen, *Rec. trav. chim.*, **82**, 90 (1963).

Okawara, *et al.*, also suggested that linear dimethyltin cations exist in certain compounds,[19] and, although Beattie and Gilson[21] questioned the existence of free cations, they did suggest bridging might occur in the dialkyltin carboxylates and fluorides which could lead to linear SnC_2 skeletons.

In an effort to understand better the nature of the proton-transfer reactions of the aquodimethyltin(IV) cation and to resolve the discrepancy in the interpretation of the polycondensation reactions[10] and the aqueous solution coupling constant data,[12] we decided to undertake a study of the Raman spectra of aqueous solutions of dimethyltin compounds. If the tin orbitals used to bond the two methyl groups are essentially sp hybrids, *i.e.*, if the cation is linear in solution, and if strong solvent–cation interactions are absent, the effective point group with free internal rotation should be D_{3d}.[22] Since there is effectively a center of symmetry, this would lead to a rather simple spectrum with six Raman active lines. If the C–Sn–C angle is less than 180°, the point group, again assuming weak solvent–cation interactions, is C_{2v}. In this case all nineteen fundamentals (21 with restricted rotation) are Raman active, and a considerably more complicated spectrum should be obtained.

Experimental

Preparation of Solutions.—Solutions of dimethyltin perchlorate and nitrate were prepared by dissolving dimethyltin oxide prepared as described earlier[10] in reagent standard perchloric and nitric acids. Dimethyltin dichloride solutions were prepared by dissolving dimethyltin dichloride[10] in water or standard HCl. The solutions contained about 0.1 M excess acid to repress hydrolysis of the dimethyltin cation. Solutions of dimethyltin nitrate in D_2O were prepared by dissolving anhydrous $(CH_3)_2Sn(NO_3)_2$ in 99.5% D_2O obtained from the Isomet Corp. The anhydrous nitrate was obtained by dehydration of solutions of the nitrate in H_2O in a vacuum desiccator over P_4O_{10}. $NaClO_4$ and $NaNO_3$ solutions were prepared from reagent grade chemicals. In order to obtain good spectra near the exciting line, the solutions were clarified as described earlier for studies on Rayleigh scattering[23] by passing them through ultra filters. Since some difficulty was experienced with fluorescence of the solutions, they were saturated with oxygen, which was found fairly effective in quenching the fluorescence.

Raman Spectra.—The Raman spectra were recorded photoelectrically with a Cary Model 81 spectrophotometer. The scan rate was 0.5 or 2.5 cm.⁻¹/sec. except that accurate determinations of the line frequencies were made with a scan rate of 0.05 cm.⁻¹/sec. The frequency scale of the instrument was calibrated with spectra of carbon tetrachloride and benzene, and the frequencies are believed to be correct within ±2 cm.⁻¹ for sharp lines. For broad or weak lines, the errors may be greater. Most of the spectra were obtained with 7-mm. Raman tubes having an illuminated length of 20 in. which are used in the lamp housing designed for gas cells. In some cases when small sample volumes were required, the solutions were sealed in specially made 6-mm. tubes having an illuminated length of *ca.* 8. in. The 4358 Å. exciting line was used for all measurements. The filter solution consisted of 40 g. of Cyasorb UV-24 and 2 g. of ethyl violet per gallon of isopropyl alcohol.

Depolarization ratios were determined using the method originally suggested by Edsall and Wilson[24] according to the proce-

dure of Crawford and Horowitz.[25] The observed depolarization ratios were found to be larger than the absolute values by measurements on carbon tetrachloride: found $\nu_{1}\rho$ = 0.306, $\nu_{2}\rho$ = 1.02, $\nu_{3}\rho$ = 1.05, $\nu_{4}\rho$ = 1.02; lit.[25] 0.046, 0.857, 0.857, and 0.857. Since all of the depolarized lines in the dimethyltin spectra were of rather low intensity in comparison to the polarized lines, it was difficult to correct the observed depolarizations by the usual procedure of normalizing to a depolarized line.

Infrared Spectra.—The infrared spectra of the aqueous solutions were determined with a Perkin-Elmer Model 521 grating spectrometer. Specially made, demountable cells with Harshaw Chemical Co. single crystal silver chloride windows were employed. Silver spacers 15 μ in thickness were used, although the path length was not accurately reproducible because of the softness of the windows. As determined from the interference fringes, the path length was typically *ca.* 14.7 μ. Because of the high solvent absorption, the spectra were usually run with solvent in the reference beam and automatic gain control or with a screen in the reference beam.

Proton N.m.r. Spectra.—The proton n.m.r. measurements were made with a Varian DP-60 spectrometer at 56.4 Mc./sec. The sample temperature was approximately 28°. The coupling constants were determined with the side-band technique and are believed to be accurate to ±1 c.p.s.

Results

Perchlorate Solutions.—Since the earlier e.m.f. studies on the proton-transfer and condensation equilibria of the dimethyltin cation had been made with a perchlorate ionic medium, the initial Raman measurements were also made on dimethyltin perchlorate solutions. Good quality spectra could be obtained with concentrations as low as 1 M. The nine observed Raman shifts are given in Table I. For comparison,

ν ClO_4^- (cm.⁻¹)	ν $[(CH_3)_2Sn]^{+2}$ (cm.⁻¹)	ν $(CH_3)_2Cd$ (cm.⁻¹)
	185 m	150 ?
463 m		
	530 vs	464–468 or 495
630 m		
932 vs		
1125 w		
	1228 m	1128–1129
	2935 s	2898–2902
	3025 m, bd	2963–2968

[a] v, very; s, strong; m, medium; w, weak; bd, broad; p, polarized; dp, depolarized. [b] Data of Fehér, Kolb, and Leveranz, ref. 26.

the Raman shifts are given for the isoelectronic molecule dimethylcadmium.[26] The perchlorate lines were very similar to those obtained for solutions of $NaClO_4$ and also essentially the same as those reported by Goggin and Woodward[27]: ν_1 (A_1) 940 cm.⁻¹ vs, p; ν_2 (E) 464 cm.⁻¹ m, dp; ν_3 (F_2) 1115 cm.⁻¹ mw, bd, dp; ν_4 (F_2) 630 cm.⁻¹ m, dp. In particular, the absence of splitting or broadening of the doubly and triply degenerate modes indicates that there is no strong complexing

(21) I. R. Beattie and T. Gilson, *J. Chem. Soc.*, 2585 (1961).
(22) R. P. Bauman, *J. Chem. Phys.*, **24**, 13 (1956).
(23) W. H. Nelson and R. S. Tobias, *Inorg. Chem.*, **2**, 985 (1963).
(24) J. T. Edsall and E. B. Wilson, *J. Chem. Phys.*, **6**, 124 (1938).

(25) B. L. Crawford, Jr., and W. Horowitz, *ibid.*, **15**, 268 (1947).
(26) F. Fehér, W. Kolb, and L. Leveranz, *Z. Naturforsch.*, **2a**, 354 (1947).
(27) P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **58**, 1495 (1962).
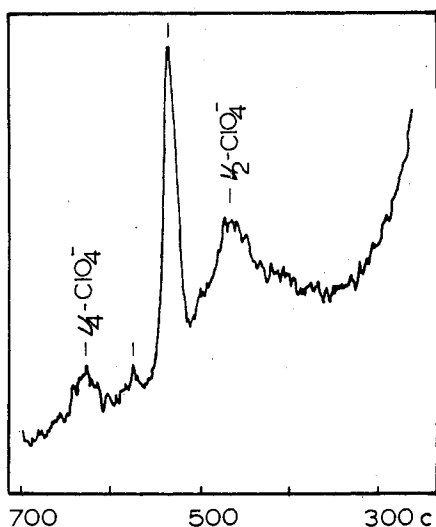
Fig. 1.—Raman spectrum of 0.1 M (CH$_3$)$_2$Sn(ClO$_4$)$_2$ titrated to $\bar{n}_{OH} = 1$.

of the dimethyltin cation by perchlorate. These solutions were particularly prone to fluoresce, and so no measurements were made of the state of polarization of the lines. It has also been observed that pure, liquid (CH$_3$)$_2$SnCl$_2$ gives rather intense background radiation.[5]

Raman shifts were also determined for 0.1 M solutions of (CH$_3$)$_2$Sn(ClO$_4$)$_2$ which had been neutralized so that on the average one proton had been transferred from the aquo cation. Under these conditions most of the dimethyltin is present as the mononuclear conjugate base or its dimer. A new line appeared in the spectrum at 580 cm.$^{-1}$, and this is shown in Fig. 1. Because of the low solubility of the conjugate base, it was impossible to use more concentrated solutions, and so the spectrum is not of high quality. Nevertheless, even at this low concentration, the weak 580 cm.$^{-1}$ line was reproducible.

Nitrate Solutions.—Because of the difficulties with fluorescence of the perchlorate solutions, Raman spectra were obtained for aqueous dimethyltin nitrate. The spectrum of 1 M (CH$_3$)$_2$Sn(NO$_3$)$_2$ consisting of eight lines is shown in Fig. 2. The presence of free nitrate ions in the solution is indicated by the similarity of the nitrate lines to those of the free nitrate ion, ν_1 (A$'_1$) 1050; ν_3 (E$'$) 1390; ν_4 (E$'$) 720 cm.$^{-1}$.[28] There was no evidence for bound nitrate ions as have been observed with aqueous solutions of CH$_3$HgNO$_3$.[27] The eight observed Raman shifts together with the integrated intensities and the observed depolarization ratios are given in Table II.

Chloride Solutions.—The Raman spectra of 1 M (CH$_3$)$_2$SnCl$_2$ consisted of five well-defined lines corresponding to those listed for the cation in Tables I and II. In addition a very weak line was observed at *ca.* 587 cm.$^{-1}$, weaker but similar to that found for the [(CH$_3$)$_2$SnOH]$^+$ solutions. This line became much more intense in the presence of excess hydrochloric acid, and another line appeared at 325 cm.$^{-1}$. In ad-
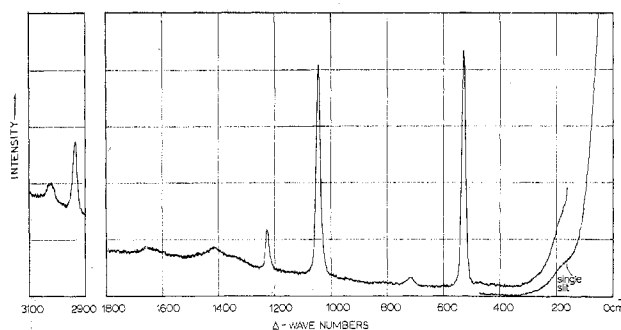
(28) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, Princeton, N. J., 1945, p. 178.

Fig. 2.—Raman spectrum of 1.0 M (CH$_3$)$_2$Sn(NO$_3$)$_2$.

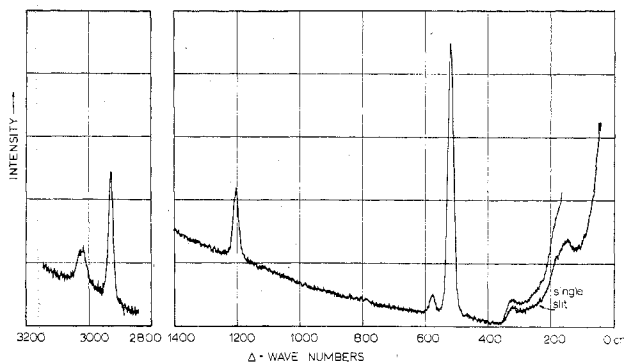
Fig. 3.—Raman spectrum of 1.0 M (CH$_3$)$_2$SnCl$_2$ in ~9 M HCl.

TABLE II
RAMAN SPECTRA OF 1 M AQUEOUS SOLUTIONS OF DIMETHYLTIN NITRATE

ν NO$_3$$^-$ (cm.$^{-1}$)	$A\nu^a$	ρ^b	ν [(CH$_3$)$_2$Sn]$^{+2}$ (cm.$^{-1}$)	$A\nu^a$	ρ^b
			180	363	1.00
			529	1510	0.444
718	96	1.00			
1045	1527	0.390			
			1226	229	0.873
1415	361	0.866			
			2933	470	0.336
			3020	268	1.51

^{a} $A\nu$ is the integrated intensity (cm.$^{-1}$ × % deflection).
^{b} Observed depolarization ratio; uncorrected.

dition, the broad depolarized line at *ca.* 180 cm.$^{-1}$ was intensified considerably. The spectrum for a 1 M solution with ~9 M HCl is shown in Fig. 3. The frequencies are tabulated together with all of those for pure liquid (CH$_3$)$_2$SnCl$_2$[5] in Table III.

TABLE III
RAMAN SPECTRA FOR 1 M AQUEOUS SOLUTIONS OF DIMETHYLTIN DICHLORIDE IN ~9 M HCl AND FOR PURE, LIQUID DIMETHYLTIN DICHLORIDE

ν solution (cm.$^{-1}$)	$A\nu$	ρ	ν (CH$_3$)$_2$SnCl$_2$(l)^a (cm.$^{-1}$)
175	2848	1.00	135 vs
325	307	0.570	344 s
518	1961	0.401	521 vs
577	140	1.00	566 m
1204	533	0.840	1211 m
2930	843	0.329	2928 m
3020	547	1.20	3010 m

^{a} Data of Edgell and Ward (ref. 5), no depolarization ratios given because of high background radiation.

Infrared Spectra.—In order to observe the infrared spectra of the dimethyltin salts in water, it was necessary to employ both H_2O and D_2O solutions because of the intense solvent absorption. As a result of the polarity of the solvent, the lines were all rather broad, and within the experimental error the frequencies were the same for both the nitrate and chloride solutions. The data are tabulated in Table V. The band observed at *ca.* 580 cm.$^{-1}$ was reproducible, but unfortunately at lower frequencies the combined absorption of the AgCl windows and the D_2O or H_2O was sufficiently great to prevent any observations. Both light and heavy water have intense absorptions due to librational modes at *ca.* 500 and 525 cm.$^{-1}$, respectively.[29]

Proton N.m.r.—Table IV lists the coupling constants determined for aqueous solutions of dimethyltin perchlorate and the dimethyltin chloride solution containing excess chloride ion for which the Raman spectra

TABLE IV

COUPLING CONSTANTS FOR DIMETHYLTIN COMPOUNDS

Compd., concn., and solvent	$J(^{117}Sn-CH_3)$, c.p.s.	$J(^{119}Sn-CH_3)$, c.p.s.	% s-character
$(CH_3)_2Sn(ClO_4)_2$, 2 M, H_2O	102[a]	106[a]	49
$(CH_3)_2Sn(C_5H_7O_2)_2$, 8%, CDCl$_3$	95.0[a]	99.3[a]	46
$(CH_3)_2Sn(OCH_3)_2$, 1.5 M, CCl$_4$	71.3[b]	74.4[b]	34
$(CH_3)_2SnCl_2$, 14%, CCl$_4$	66.6[c]	69.7[c]	32
$(CH_3)_2SnCl_2$, 9 M, HCl	92.5[a]	97.5[a]	45

[a] This work. [b] Gerrard, Leane, Mooney, and Rees (ref. 30). [c] Holmes and Kaesz (ref. 12).

were determined. Data are also given for an octahedral coordination compound of dimethyltin in which the methyl groups are believed to occupy *trans* positions, bis(acetylacetonato)dimethyltin(IV); dimethoxydimethyltin(IV),[30] which is presumed to be tetrahedral in solution; and dimethyltin dichloride. The table also lists the per cent s-character in the tin orbitals used to bond the methyl carbons as calculated with the linear relation between coupling constant and per cent s-character suggested by Holmes and Kaesz.[12] No measurable broadening of the proton resonance line was observed in concentrated solutions of dimethyltin salts in H_2O or in D_2O containing small amounts of H_2O, thus indicating rapid exchange of the protons in the coordinated water molecules with the bulk solvent.

Discussion

The simplicity of the cation spectra and the pronounced similarity to those of other ions and molecules with linear skeletons, *e.g.*, $[(CH_3)_2Tl]^+$,[31] $(CH_3)_2Hg$,[31-34] $(CF_3)_2Hg$,[35] and, as shown in Table I, $(CH_3)_2Cd$,[33,34]

(29) G. E. Walrafen, *J. Chem. Phys.*, **36**, 1035 (1962).
(30) W. Gerrard, J. B. Leane, E. F. Mooney, and R. G. Rees, *Spectrochim. Acta*, **19**, 1964 (1963).
(31) P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 1591 (1960).
(32) L. A. Woodward, *Spectrochim. Acta*, **19**, 1963 (1963).
(33) H. S. Gutowsky, *J. Chem. Phys.*, **17**, 128 (1949).
(34) H. S. Gutowsky, *J. Am. Chem. Soc.*, **71**, 3194 (1949).
(35) A. J. Downs, *J. Chem. Soc.*, 5273 (1963).

which is isoelectronic with $[(CH_3)_2Sn]^{+2}$, all point to the linear structure with point group D_{3d}. As was noted earlier, if the skeleton were bent all 19 fundamentals (with free rotation) would be both Raman and infrared active. In practice, because of the heavy tin atom, there is likely to be much accidental degeneracy, and this has been noted in the Raman spectrum of $(CH_3)_2SnCl_2$.[5] Nevertheless the presence of but a single line in the tin–carbon stretching region from 500 to 600 cm.$^{-1}$ strongly indicates that the cation has a linear Sn–C$_2$ skeleton in aqueous solution. It is possible but unlikely that the C–Sn–C angle is somewhat less than 180°, for under such conditions the spectrum can be expected to differ only slightly from that for D_{3d} symmetry.[36]

A complete assignment of the fundamentals of the aquodimethyltin cation is given for both the infrared and Raman in Table V. Approximate descriptions of

TABLE V

ASSIGNMENT OF FUNDAMENTALS FOR THE AQUODIMETHYLTIN(IV) ION, EFFECTIVE POINT GROUP D_{3d}

Approximate description of mode			Raman (cm.$^{-1}$)	Infrared (cm.$^{-1}$)
CH$_3$ stretch (sym.)	ν_1	(A_{1g})	2933	i.a.[a]
CH$_3$ deform. (sym.)	ν_2	(A_{1g})	1226	i.a.
SnC$_2$ stretch (sym.)	ν_3	(A_{1g})	529	i.a.
(CH$_3$ torsion[b])	ν_4	(A_{1u})	...	...
CH$_3$ stretch (sym.)	ν_5	(A_{2u})	i.a.	2935[c]
CH$_3$ deform. (sym.)	ν_6	(A_{2u})	i.a.	1202[d]
SnC$_2$ stretch (antisym.)	ν_7	(A_{2u})	i.a.	582[d]
CH$_3$ stretch (antisym.)	ν_8	(E_g)	3020	i.a.
CH$_3$ deform. (antisym.)	ν_9	(E_g)	e	i.a.
CH$_3$ rock	ν_{10}	(E_g)	e	i.a.
CH$_3$ stretch (antisym.)	ν_{11}	(E_u)	i.a.	3015[c]
CH$_3$ deform. (antisym.)	ν_{12}	(E_u)	i.a.	1403[d]
CH$_3$ rock	ν_{13}	(E_u)	i.a.	790[c]
SnC$_2$ bend	ν_{14}	(E_u)	i.a. (180[f])	...

[a] i.a. = inactive. [b] Absent for free rotation. [c] Measured in D_2O solutions. [d] Measured in H_2O solutions. [e] Not observed in pure, liquid $(CH_3)_2SnCl_2$ because of the very low intensity. [f] Observed with most $(CH_3)_2M$ compounds.

the modes are also given. The representations of these internal coordinates are easily obtained with group theory and have been given by Goggin and Woodward.[31] Our numbering of the vibrations is slightly different to conform to the character table in Wilson, Decius, and Cross[37] and is in agreement with that of Downs.[35]

There are several features of these spectra which merit discussion. First, neither the Raman active antisymmetrical methyl deformation frequency ν_9 nor the methyl rocking frequency ν_{10} was observed; however, these give very weak lines in the Raman spectra of the heavier group IV elements. Neither of these vibrations gives a Raman line of measurable intensity even in pure, liquid $(CH_3)_2SnCl_2$, and so it is not surprising that they were not observed in the solution spectra.

(36) R. F. Curl and K. S. Pitzer, *J. Am. Chem. Soc.*, **80**, 2371 (1958).
(37) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955.

Secondly, a weak, broad depolarized line appears in the perchlorate and nitrate spectra at *ca.* 180 cm.$^{-1}$. This has been assigned to the Sn–C$_2$ bending mode, although this is formally Raman inactive for D$_{3d}$ symmetry. All of the analogous linear (CH$_3$)$_2$M molecules and ions show this feature. This apparent breakdown of the selection rules for D$_{3d}$ symmetry has been discussed for (CH$_3$)$_2$Hg by Gutowsky[34] and recently by Woodward.[32]

It has proved possible to make a complete vibrational assignment for the aquodimethyltin cation without any consideration of the interaction of the cation with water molecules. The absence of any Raman shifts attributable to tin–oxygen bonds indicates that the water molecules in the first coordination sphere must be attached by highly polar bonds, *i.e.*, by essentially ion–dipole attractions. Presumably there are four water molecules coordinated in the equatorial plane. Although the absence of any appreciable covalent character in the bonds to water molecules has also been observed for aqueous [(CH$_3$)$_2$Tl]$^+$, it is somewhat more surprising in [(CH$_3$)$_2$Sn]$^{+2}$. While the dimethylthallium ion is a very weak aquo acid, there is a pronounced enhancement of the acidity of water molecules coordinated to the dimethyltin ion. This is shown by a comparison of the first acid dissociation constants; [(CH$_3$)$_2$Tl]$^+$, $K_{11}^* \simeq 10^{-13}$ (calculated from the stability constant for the monohydroxo complex, log K_{11} = 1.04),[38] and [(CH$_3$)$_2$Sn]$^{+2}$, $K_{11}^* = 10^{-3.1}$ (0.1 M NO$_3^-$ medium).[39] Apparently the only aquo ion for which a metal–oxygen bond has sufficient covalent character to give a line in the Raman spectrum is [CH$_3$HgOH$_2$]$^+$,[27] $K_{11}^* = 10^{-4.4}$ [40,41] (calculated from the stability constant of the monohydroxo complex). Here a strong bond to one axial water molecule is indicated, and the Raman spectrum can be assigned on the basis of C$_{3v}$ symmetry, the water protons having little effect. This indicates that any additional coordinated water also must be bound by essentially ion–dipole forces.

It seems likely that dissolution of the heavier organometallic halides in polar solvents will generally proceed with an increase in the coordination number and a maximization of the metal s-character in the orbitals used in bonding to carbon. This also has been indicated by infrared studies by Matwiyoff and Drago[42] on (CH$_3$)$_3$SnCl, which appears to have a planar Sn–C$_3$ skeleton in polar, nonaqueous solvents.

The C–H stretching frequencies are quite high in (CH$_3$)$_2$Sn^{+2} although very similar to the values for (CH$_3$)$_2$Tl$^+$.[31] The symmetrical methyl deformation frequency is also low, and these factors indicate a rather large amount of s-character is present in the carbon orbitals used to bind the hydrogen atoms. These frequencies are rather similar to those observed from

the infrared spectra of methyl iodide, C–H symmetrical stretch 2970 (2950 corrected for Fermi resonance) and CH$_3$ symmetrical deformation 1252 cm.$^{-1}$.[43] All of the corresponding frequencies in dimethylcadmium seem to be lower than in the dimethyltin ion, and it appears rather easy to stretch and bend the C–H bonds as well as the Cd–C bonds. The factors leading to these changes are not clear, although the increased orbital electronegativity of Sn(IV) compared to Cd(II) is probably involved.

The most obvious explanation of the new line in the solutions of approximate stoichiometry [(CH$_3$)$_2$SnOH]$^+$ is that this is due to the antisymmetrical tin–carbon stretching frequency. Transfer of a proton from a coordinated water molecule will presumably result in a strengthening of one tin–oxygen bond because of the increased donor character of a hydroxo group compared to a water molecule. The symmetry must decrease to no greater than C$_{2v}$, and the antisymmetrical stretch becomes Raman allowed. It is also likely that the formation of a stronger tin–oxygen bond will result in a distribution of the s-character among three bonds rather than two, *i.e.*, that the C–Sn–C angle will decrease appreciably. This would account for the high stability of the binuclear complex [(CH$_3$)$_2$Sn(OH)$_2$-Sn(CH$_3$)$_2$]$^{+2}$ and for (CH$_3$)$_2$Sn(OH)$_2$ at higher pH values as was observed in the e.m.f. studies on the aquo acidity of the dimethyltin ion.[10] Because of the large mass of the tin atom, it is unlikely that the simple transfer of a proton from one of the coordinated water molecules with no tin–carbon bond bending would lead to the antisymmetrical stretching vibration appearing in the Raman spectrum with appreciable intensity. Considering the fact that the hydroxo group will still be hydrogen bonded to the bulk solvent molecules, such a proton transfer should have relatively little effect on the variation of the cation polarizability with the tin–carbon stretching vibrations.

No line attributable to a tin–oxygen stretching vibration was observed for the hydroxo complex, but the doubly and triply degenerate perchlorate vibrations ν_2 and ν_4 gave rise to rather broad lines in this region. In addition, the very broad 500 cm.$^{-1}$ librational mode of water[29] is intensified considerably in these spectra.

Raman spectra provide an excellent technique for the study of interactions of ions like [(CH$_3$)$_2$Sn]$^{+2}$ not only with the solvent but also with different ligands. The vibrational spectrum of the cation itself is susceptible to minor perturbations, manifested as small shifts in the frequencies, by ligands bound by even simple hard sphere Coulombic or ion–dipole forces, but there should be much more pronounced changes when ligands are coordinated by bonds having appreciable covalent character. This has already been indicated in the case of the monohydroxo complex in perchlorate solutions and is shown much more clearly by the spectra of the dimethyltin ion in the presence of high concentrations of chloride ion. Earlier studies had indicated that the monochloro complex of dimethyltin was appreciably

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stable.[44] It is very unlikely that appreciable concentrations of molecular $(CH_3)_2SnCl_2$ exist in aqueous solution, and, indeed, the addition of high concentrations of a soluble chloride causes precipitation of $(CH_3)_2SnCl_2$. The appearance of a new polarized line at 325 cm.$^{-1}$ in solutions containing excess chloride ion at approximately the frequency of the tin-chlorine stretch in trimethyltin chloride[5] confirms the presence of the chloro complex. In addition a new depolarized Raman line appears at 577 cm.$^{-1}$ corresponding closely to the antisymmetrical SnC_2 stretching frequency in $(CH_3)_2SnCl_2$,[5] and this indicates the loss of the effective center of symmetry as a result of complexing of the cation. As discussed above, it is probable that the tin atomic s-character is now distributed over the three bonds which have appreciable covalent character. The fact that the antisymmetrical stretch is clearly visible in the chloride solutions and completely absent from the spectra of the perchlorate and nitrate solutions would seem to confirm the linear skeletal structure proposed for the simple aquo cation. Finally, the complexing by chloride ion results in a pronounced intensification of the broad, depolarized line at *ca.* 180 cm.$^{-1}$ which has been assigned in the aquo ion to the SnC_2 bending mode. This mode, which as noted above is Raman inactive for D_{3d}, becomes active for C_{2v} symmetry, and, by analogy with $(CH_3)_2SnCl_2$, all of the skeletal bending modes in $[(CH_3)_2SnCl]^+$ are assigned to this broad, intense line. Approximate descriptions of the modes, the symmetry species, and the selection rules for $[(CH_3)_2SnCl]^+$ are given in Table VI. Assignments of the Raman shifts are given in Table VII.

TABLE VI
Vibrational Modes, Symmetry Species, and Selection Rules
for $[(CH_3)_2SnCl]^+$, Effective Point Group C_{2v}

Approximate description of mode	Symmetry species[a]			
	A_1	A_2	B_1	B_2
CH_3 stretch (antisym.)	ν_1	ν_9	ν_{13}	ν_{18}
CH_3 stretch (sym.)	ν_2			ν_{19}
CH_3 deform. (antisym.)	ν_3	ν_{10}	ν_{14}	ν_{20}
CH_3 deform. (sym.)	ν_4			ν_{21}
CH_3 rock	ν_5	ν_{11}	ν_{15}	ν_{22}
$Sn-C_2$ stretch	ν_6			ν_{23}
SnCl stretch	ν_7			
$C-Sn-Cl$ deform.	ν_8			ν_{24}
$C_2-Sn-Cl$ out-of-plane deform.			ν_{16}	
CH_3 torsion		$\nu_{12}{}^b$		$\nu_{17}{}^b$

[a] Activity: A_1, Raman polarized and infrared; A_2, Raman and infrared; B_1, Raman and infrared; B_2, Raman and infrared. [b] Absent for free rotation.

TABLE VII
Vibrational Assignments for the
Raman Spectrum of $[(CH_3)_2SnCl]^+$

Obsd. frequency, cm.$^{-1}$	Assignment
3025 dp	ν_1, ν_9, ν_{13}, ν_{18}
2930 p	ν_2, ν_{19}
1204 p	ν_4, ν_{21}
577 dp	ν_{23}
518 p	ν_6
325 p	ν_7
175 dp	(ν_8), ν_{24}, ν_{16}

The coupling constant data given in Table IV are in accord with essentially sp hybridization for the simple aquodimethyltin cation. The coupling constants determined for the aquo ion are also rather similar to those measured for the octahedral chelate of the dimethyltin ion, bis(acetylacetonato)dimethyltin(IVi) which is believed to have the methyl groups in approximately *trans* positions. As an indication that the large amount of s-character in the tin orbitals bonding the methyl groups is not in some way only a result of the higher electronegativity of oxygen compared to carbon,[45] the coupling constants for dimethoxydimethyltin are found to be much smaller and rather close to the values for dimethyltin dichloride. The methoxide is presumably monomeric and tetrahedral in CCl_4 solution.

It is, perhaps, not surprising in view of the extensive rehybridization which accompanies the formation of the aquo ion that the linear relation observed by Brown and Morgan between the $J(^{119}Sn-CH_3)$ values and the symmetrical tin–carbon stretching frequency[46] is not obeyed here. The trimethyltin aquo ion, $[(CH_3)_3Sn]^+$, does seem to fall on the straight line generated by a variety of methyltin compounds, but the rehybridization which occurs when trimethyltin chloride dissolves in water is considerably less.

These coupling constant data would tend to rule out any appreciable utilization of the $5d_{z^2}$ tin orbital in the bonding of the methyl groups in $[(CH_3)_2Sn]^{+2}$, *e.g.*, by the use of $(sd_{z^2} + p_z)$ hybrids. This is in agreement with the fact that the very large d–s separation in Tl(III), Sn(IV), etc., would render such orbital mixing unlikely, and so such hybridization cannot be used to explain the absence of strong, covalent bonds to the equatorial water molecules. The coupling constant data also infer that the environment about the tin atom in the dimethyltin aquo ion and in the acetylacetone complex must be similar, *i.e.*, the two acetylacetonato groups must be coordinated by bonds which are predominantly ionic.

The maximization of the metal s-character in the bonds to carbon in aquo organometallic ions seems to be the rule, for it also has been found that $[(CH_3)_2Pb]^{+2}$,[47] as well as the isoelectronic $[(CH_3)_2Tl]^+$,[31] ions have similar linear structures in aqueous solution. While the existence of linear dimethylthallium(III) cations is well known in crystals,[48] the existence of linear dimethyltin(IV) ions in crystals has not yet been demonstrated by X-ray diffraction. By analogy with the aquo complex, it would appear quite likely that linear dimethyltin groups do exist in $(CH_3)_2SnF_2$ as suggested by Okawara, *et al.*,[19] and by Beattie and Gilson.[21]

It is interesting in the light of the Raman evidence for bond bending in going from the aquo ion to the monochloro complex that the coupling constants indicate that the s-character in the tin orbitals bonding the methyl groups decreases by only about 9% from $(CH_3)_2$-

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$Sn(ClO_4)_2$ to $[(CH_3)_2SnCl]^+$ in 9 M HCl. This relatively small decrease may be a result of the rather high electronegativity of chlorine.[45]

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The Polymeric Nature of Titanium Tetraethoxide in Solution.
I. Cryoscopic Studies in Benzene

BY D. C. BRADLEY AND C. E. HOLLOWAY

In carefully dried benzene the molecular weight of $Ti(OC_2H_5)_4$ is independent of concentration over the range 2.0–100.2 $\times$ 10^{-3} m. The number average degree of polymerization of 2.82 suggests that a single trimeric species is present in solution, contrary to the tetrameric nature of the crystalline solid. No evidence for a time-dependent depolymerization was found and it is suggested that early reports of such behavior and of a concentration dependence of molecular weight resulted from hydrolysis. Experiments with slightly wet benzene (4×10^{-3} m water) demonstrated that hydrolysis causes an apparent decrease in molecular weight with decrease in concentration.

Although several workers have studied the colligative properties of titanium tetraethoxide in organic solvents, certain features of these results demanded further investigation.

For example, Caughlan, et al.,[1] found by cryoscopy in benzene that the degree of polymerization was concentration dependent, increasing from unity at low concentration to a maximum of three.

On the other hand, Bradley, et al.,[2] found that the degree of polymerization was constant at 2.4 over a reasonable concentration range in boiling benzene. Recently, Ibers[3] has reported preliminary details of the crystal structure of $Ti(OC_2H_5)_4$ as determined by X-ray diffraction with the very interesting conclusion that the substance is tetrameric in the solid state. At the same time Martin and Winter[4] reported cryoscopic molecular weight measurements over a wide concentration range in benzene and confirmed the concentration dependence of the degree of polymerization at low concentrations. Although their data appear to indicate a trimeric ceiling at higher concentrations, they claim that the results are not adequately described by a monomer–trimer equilibrium but need the presence of a tetrameric species too.

Perhaps the most remarkable results are those due to Nesmeyanov, et al.,[5] who presented evidence suggesting that the degree of polymerization of titanium tetraethoxide and other titanium alkoxides determined cryoscopically in benzene solution slowly decreased with time until the monomeric state was reached. Moreover they claimed that the rate of depolymerization increased with increase in temperature and they deduced an "activation energy of dissociation" of 8.0 kcal./mole for titanium tetraethoxide.

We were skeptical of these results and in checking the behavior of titanium ethoxide in benzene solution have found some interesting results which we hope will now clarify the situation.

Experimental

The main purpose of this investigation was to perform cryoscopic measurements on benzene solutions of $Ti(OC_2H_5)_4$ with rigorous precautions to prevent hydrolysis. The cryoscopic method is particularly vulnerable to this source of contamination because atmospheric moisture is readily condensed into the solution when the freezing point determinations are made. If a positive pressure of say dry nitrogen is used to prevent the ingress of moisture considerable errors can be caused by evaporation of the solvent. We used an all-glass double-walled vessel containing a Sargent S-81630 thermistor sealed-in with Fisher Sealit, and a glass-covered magnetic stirrer. The temperature of the system was measured using a thermistor bridge and a Philips PR4069M/04 recorder.

The pure solvent and solute were introduced through the thermistor joint which was then sealed. These filling operations were conducted in an atmosphere of dry nitrogen in a drybox.

Benzene was dried first azeotropically with ethanol and then over Molecular Sieve 4A which had been freshly dried by heating at 200° *in vacuo* for about 4 hr. Titanium tetraethoxide prepared by the usual method[2] was distilled *in vacuo* and the supercooled liquid was added from a special weight pipet. Although this method may not completely exclude moisture due to the filling procedure, sealing of the apparatus must prevent progressive hydrolysis.

The thermistor was calibrated by determining the freezing points of solutions of known concentrations of fluorene in benzene in

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