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Studies by Vibrational Spectroscopy of Octahedral Tin(IV) Complexes of the Type $(CH_3)_2SnX_4{}^{2-}$ ($X^- = F^-, Cl^-, Br^-, NCS^-$). Normal Coordinates and Evidence for a *cis* Effect[1,2]

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Raman and infrared spectra have been obtained for the complex organotin(IV) anions $(CH_3)_2SnX_4{}^{2-}$ ($X^- = F^-, Cl^-, Br^-, NCS^-$) and for comparison $(CH_3)_2SnF_2$. The Raman spectrum of the difluoride is very similar to that of the aquodimethyltin(IV) cation, and the very low Sn–F stretching intensity indicates that these bonds are essentially hard-sphere coulombic interactions. The spectra of the thiocyanate complex indicate that the ligand is coordinated *via* the nitrogen atom. Normal-coordinate calculations were carried out for the $(CH_3)_2SnX_4{}^{2-}$ and $SnX_6{}^{2-}$ ($X^- = F^-, Cl^-, Br^-$) anions using a Urey–Bradley force field. The skeletal SnC_2 stretching frequencies and force constants decrease in the sequence $F^- > Cl^- > Br^-$ suggesting that there is some covalency in the tin–halogen bonds. Replacement of two halides of $SnX_6{}^{2-}$ with two methide ions leads to decreases in the Sn–X stretching force constants. This effect is greatest with $X^- = F^-$ and virtually negligible with Br^-.

Introduction

The dimethyltin(IV) moiety forms a large number of coordination compounds where the total coordination number for tin is 6. In general, when the ligands other than the carbanions are equivalent and highly electronegative, the *trans* isomer is the stable one. The simplest example of this is dimethyltin difluoride where each fluoride bridges between tin atoms giving a coordination number of 6 for tin and a rather short Sn–C bond length of 2.06 Å.[4]

Dialkyltin dihalides react with an excess of halide ion to produce the six-coordinate tin anions $R_2SnX_4{}^{2-}$. In 1910, Pfeiffer[5] reported the isolation of such anions as the pyridinium or quinolinium salts. Krause[6] prepared the complex fluoride $K_2[(C_2H_5)_2SnF_4]$. Reutov, *et al.*,[7] also reported the synthesis of similar anions as salts of quaternary ammonium ions.

In 1963, Beattie and McQuillan[8] noted that $(C_5H_5NH)_2[(CH_3)_2SnCl_4]$ exhibited only one tin–carbon stretching frequency in the infrared spectrum at 564 cm^{-1}, and they concluded that the compound had the *trans* structure. This structure violated the usual tendency of $SnCl_4L_2$ complexes to have the smallest ligands *cis*.[9] The *trans* structure was also assigned by Clark and Wilkins[10] in a study of $Cs_2[(CH_3)_2SnCl_4]$ and $Cs_2[(CH_3)_2SnBr_4]$, by Wilkins and Haendler[11] for $K_2[(CH_3)_2SnF_4]$, and by Wada and Okawara[12] for $[(CH_3)_4N][(CH_3)_2Sn(NCS)_4]$. No tin–halogen stretching vibrations have been reported, and it has been presumed that these were below the limit of the spectrometers employed. This suggested, by comparison with the behavior of $(CH_3)_2SnCl_2$, that the Sn–Cl stretching force constant was anomalously low.[8]

The assignment of the *trans* structure for the chloro complex has been supported by the quadrupole splitting data from Mössbauer spectra of $(C_5H_5NH)_2[(CH_3)_2SnCl_4]$.[13]

There is evidence from anion-exchange studies for the existence of low concentrations of $(CH_3)_2SnF_4{}^{2-}$ in aqueous HF solutions,[14] but, in general, it is very difficult to displace all of the water molecules from the first coordination sphere of tin. With chloride ion, the principal species found in concentrated HCl solution is $(CH_3)_2SnCl^+(aq)$.[14,15] All of these complex halogeno anions aquate very rapidly when dissolved in water.

Since we have been interested in the effect of σ-bonded carbanion ligands in the first coordination sphere of metal ions on the stereochemistry and reactivity of the complexes, we have examined the infrared and Raman spectra of several complex dimethyltin(IV) halide and pseudohalide anions. To study these effects in more detail, normal-coordinate calculations have been carried out on the $(CH_3)_2SnX_4{}^{2-}$ and $SnX_6{}^{2-}$ ($X^- = F^-, Cl^-, Br^-$) anions.

Experimental Section

General Data.—Dimethyltin oxide and dichloride were obtained from M & T Chemicals, and tetraethylammonium bromide was from Eastman Organic Chemicals. All microanalyses were made by Schwarzkopf Microanalytical Laboratory Woodside, N. Y., or Clark Microanalytical Laboratory, Urbana, Ill.

Dimethyltin Difluoride, $(CH_3)_2SnF_2$.—This compound was prepared by reaction of $(CH_3)_2SnO$ and aqueous HF. *Anal.*

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[2] Taken from a thesis submitted by C. W. H. to the Graduate School of the University of Minnesota for the Ph.D. degree, 1969.

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Calcd for $C_2H_6F_2Sn$: C, 12.9; H, 3.22; F, 20.4. Found: C, 13.0; H, 3.32; F, 20.2.

Potassium Tetrafluorodimethylstannate(IV), $K_2[(CH_3)_2SnF_4]$.—The dihydrate was prepared by the method of Wilkins and Haendler[11] which involved reaction of $(CH_3)_2SnF_2$ and $KF \cdot 2H_2O$ in aqueous solution. The large, clear, hydrated crystals were ground into small particles and stored in a desiccator over P_4O_{10} for 2 weeks to dehydrate them. *Anal.* Calcd for $K_2C_2H_6F_4Sn$: C, 7.92; H, 1.98; F, 25.0. Found: C, 8.08; H, 2.19; F, 24.5.

Cesium Tetrachlorodimethylstannate(IV) and Cesium Tetrabromodimethylstannate(IV), $Cs_2[(CH_3)_2SnX_4$ ($X^- = Cl^-, Br^-$).—These compounds were prepared essentially by the method of Clark and Wilkins.[10] To produce the chloro complex, $(CH_3)_2SnCl_2$ was allowed to react with CsCl in an ethanol–water solvent. The solid product was collected on a frit and washed with ether. *Anal.* Calcd for $Cs_2C_2H_6Cl_4Sn$: C, 4.31; H, 1.08; Cl, 25.5. Found: C, 4.45; H, 1.19; Cl, 25.6. The bromo complex was synthesized by treating $(CH_3)_2SnO$ with HBr and adding CsBr. The compound was dried under vacuum to remove traces of $(CH_3)_2SnBr_2$. *Anal.* Calcd for $Cs_2C_2H_6Br_4Sn$: C, 3.27; H, 0.82; Br, 43.5. Found: C, 3.40; H, 0.88; Br, 43.6. The unit cell for this compound was found by X-ray diffraction with a single crystal to be orthorhombic, $a = 8.340 \pm 0.012$, $b = 12.367 \pm 0.021$, $c = 12.236 \pm 0.020$ Å. The space group is either Ama2 ($C_{2v}{}^{16}$), Cmcm, or $Cmc2_1$.[16] A test for pyroelectricity was positive indicating an acentric space group. The volume of the unit cell is 1262 Å^3 compared to 1260 Å^3 for Cs_2SnBr_6[17] which has four formula units per cell suggesting that the same is true for the organotin compound.

Tetramethylammonium[18] and Tetraethylammonium Tetraisothiocyanatodimethylstannate(IV), $R_2[(CH_3)_2Sn(NCS)_4]$ ($R = (CH_3)_4N^+, (C_2H_5)_4N^+$).—These thiocyanate complexes were synthesized by the procedure of Cassol, Portanova, and Barbieri;[19] mp ($R = (C_2H_5)_4N^+$) 120–122°, lit. mp 113–115°.[19] *Anal.* Calcd for $C_{14}H_{30}N_6S_4Sn$: C, 31.8; H, 5.71; Sn, 22.4. Found: C, 31.7; H, 5.98; Sn, 21.7. Calcd for $C_{22}H_{46}N_6S_4Sn$: C, 41.2; H, 7.18; N, 13.1; S, 20.0. Found: C, 38.7; H, 6.96; N, 11.5; S, 18.8. Since this microanalysis indicated less than the theoretical percentage of thiocyanate, thiocyanate was also determined gravimetrically as the silver salt.[20] *Anal.* Calcd: NCS^-, 36.2. Found: NCS^-, 40.0. The nmr spectrum of $[(CH_3)_4N]_2[(CH_3)_2Sn(NCS)_4]$ was determined in acetone solution. The ratio of the intensity of the tetramethylammonium protons to that of the dimethyltin protons was 4:1. The spin–spin coupling constants determined with an acetone solution were $J(^{117}Sn\text{–}H) = 108.0$ and $J(^{119}Sn\text{–}H) = 113.1$ Hz.

Raman Spectra.—Two instruments were used to record the Raman spectra. One was a conventional mercury arc excited Cary 81 spectrophotometer using the 4358-Å line. The second spectrophotometer employed an He–Ne laser and a Spex Model 1400 double monochromator and has been described elsewhere.[21]

With the Cary instrument, solid spectra were recorded with conical cells, while with the laser excitation a thin layer of powder was illuminated at 90° to the optical axis of the monochromator, or transillumination of the sample in a capillary was employed. The spectra of single crystals were obtained by mounting a polished crystal in a normal X-ray goniometer head and employing 90° illumination. Frequencies for sharp lines are believed accurate to ± 2 cm^{-1}.

Infrared Spectra.—Perkin-Elmer 521 and Beckman IR-12 spectrometers were used and calibration was effected with polystyrene film. Solid spectra in the 200–1300-cm^{-1} region were obtained with Nujol mulls using CsI windows, while spectra from 1300 to 4000 cm^{-1} were obtained using NaCl or KBr plates and Halocarbon oil mulls. The frequencies of sharp bands are accurate to within ± 2 cm^{-1}, while those for broad bands are within ± 5 cm^{-1}.

Proton Magnetic Resonance Spectra.—A Varian A-60 spectrometer was used. Side bands were produced by a Hewlett-Packard 3300A function generator, and a Hewlett-Packard 3734A electronic counter was used to calibrate the frequency. Coupling constants are believed to be accurate to ± 0.5 Hz.

Data and Results

The Raman and infrared spectra of $(CH_3)_2SnF_2$ with qualitative assignments are collected in Table I together with values[22] for the linear aquo cation, $(CH_3)_2Sn^{2+}$, for comparison. Figure 1 illustrates both the Raman and infrared spectra for the difluoride. The infrared frequencies are similar to those reported previously.[23] No vibrations involving totally symmetric tin–fluorine bond stretching could be detected in the Raman spectrum. Trimethyltin fluoride behaves similarly, and a broad intense band is observed in the infrared spectrum at 350 cm^{-1}, but no Raman line was found at ≥ 150 cm^{-1}.[24] The band at 140 cm^{-1}

TABLE I

INFRARED AND RAMAN FREQUENCIES[a] AND ASSIGNMENTS FOR $(CH_3)_2SnF_2$ TOGETHER WITH VALUES FOR $(CH_3)_2Sn(aq)^{2+}$ [22]

ν, cm^{-1}				
$(CH_3)_2Sn(aq)^{2+}$		$(CH_3)_2SnF_2$		
Ir	Raman	Ir	Raman	Assignment
...	185		140	δ(O–Sn–C), δ(F–Sn–C)
...	...	360 vs, b	...	$\nu(Sn\text{–}F_4)$
...	529 vs	...	532 vvs	$\nu_s(SnC_2)$
582	...	598 m	...	$\nu_{as}(SnC_2)$
790	...	785 s, b	...	$\rho_r(CH_3\text{–}Sn)$
1202	1226 m	1209 *m*	1211 *m*	$\delta_s(CH_3)$
1403	...	1410 w	...	$\delta_{as}(CH_3)$
2935	2933 s	2932 m	2928 m	$\nu_s(CH_3)$
3015	3020 m, b	3020 w, b	3019 vw	$\nu_{as}(CH_3)$

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad.

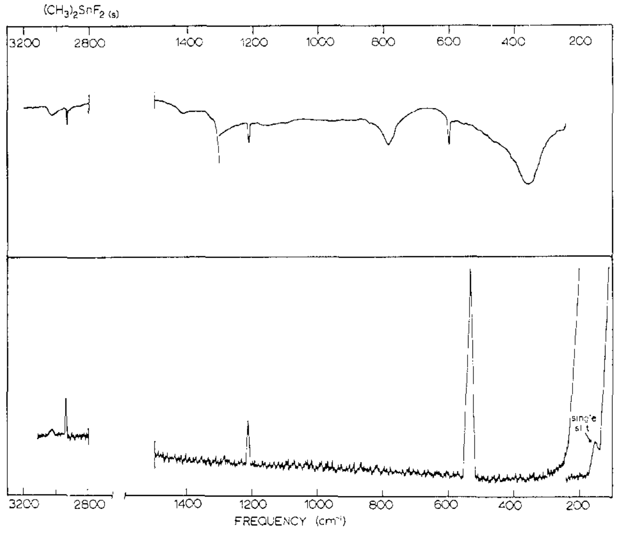

Figure 1.—Infrared and Raman spectra of $(CH_3)_2SnF_2$.

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(16) We are indebted to Miss Y. M. Chow for these measurements.

(17) R. W. G. Wyckoff, "Crystal Structures," Vol. 3, 2nd ed, Interscience Publishers, New York, N. Y., 1965, p 341.

(18) We are indebted to Mr. L. O. Johnson, an NSF Summer Participant, 1965, for the synthesis of this compound.

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TABLE II
INFRARED AND RAMAN FREQUENCIES FOR *trans*-$(CH_3)_2SnX_4^{2-}$ ($X^- = F^-, Cl^-, Br^-, NCS^-$)

ν, cm^{-1}								
$K_2[(CH_3)_2SnF_4]$		$Cs_2[(CH_3)_2SnCl_4]$		$Cs_2[(CH_3)_2SnBr_4]$		$((C_2H_5)_4N)_2[(CH_3)_2Sn(NCS)_4]$[a]		
Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Assignment
	(142 w)[b]		139 m		134 s		. . .	δ(C–Sn–X)
					183 s, 174 m			ν(Sn–Br$_4$)
			207 s, 197 m					ν(Sn–Cl$_4$)
	224 s							Lattice?
		235 s						ν_{as}(Sn–Cl$_4$)
257 s								δ(Sn–F$_4$)
347 397} vvs								ν_{as}(Sn–F$_4$)
						472 482 489 495} m		δ(NCS)
	539 vs		508 vs		498 vs		522 s	ν_s(Sn–C$_2$)
582 s		580 s		571 m		587 m		ν_{as}(Sn–C$_2$)
773 s		793 m, b		788 m, b		787 vs?		ρ_r(Sn–CH$_3$)
1195 m	1214 m	1192 vw	1203 m	1193 vw	1194 m	1194 m	. . .	δ_s(CH$_3$)
1410 w		1410 vw 1438 vw		1400 vw	1380 vvw			δ_{as}(CH$_3$)
						2037 vs 2086 s	2040 2052 2086} vvs	ν(C≡N)
2805 w								2 × 1410 cm^{-1}
2926 s, b		2930 vvw	2926 m	2930 vw	2918 m			ν_s(CH$_3$)
3001 s		3020 vvw	3023 w	3015 vvw	3017 w			ν_{as}(CH$_3$)

[a] Vibrations associated with the tetraethylammonium cation were identified from infrared and Raman spectra of $[(C_2H_5)_4N]Br$. These are not listed in the table. [b] Observed in the spectrum of a single crystal of the dihydrate.

probably involves primarily F–Sn–C angle bending, for a similar band is found at *ca.* 185 cm^{-1} with the aquo cation. The low Raman intensity of the Sn–F stretching vibrations indicates that the interaction is predominantly ionic in nature.

In Table II, the Raman and infrared spectra for the complex anions $(CH_3)_2SnX_4^{2-}$ ($X^- = F^-, Cl^-, Br^-, NCS^-$) are collected. All of the spectra are consistent only with the *trans* structure.

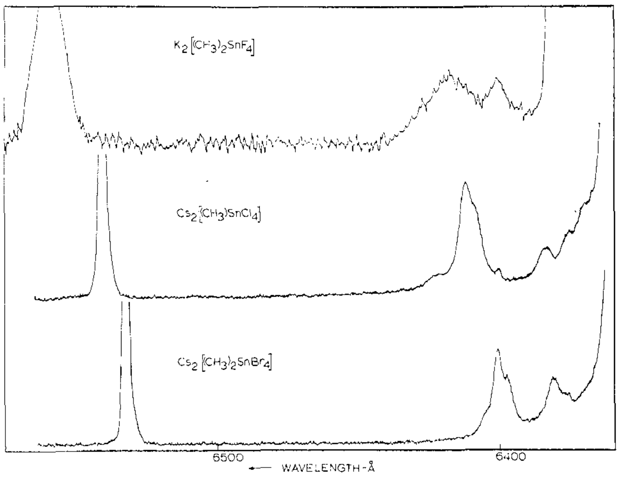

Figure 2.—Laser Raman spectra of $K_2[(CH_3)_2SnF_4]$, $Cs_2[(CH_3)_2SnCl_4]$, and $Cs_2[(CH_3)_2SnBr_4]$ excited with an He–Ne laser (6328 Å). The bands at *ca.* 6401 Å are a grating ghost.

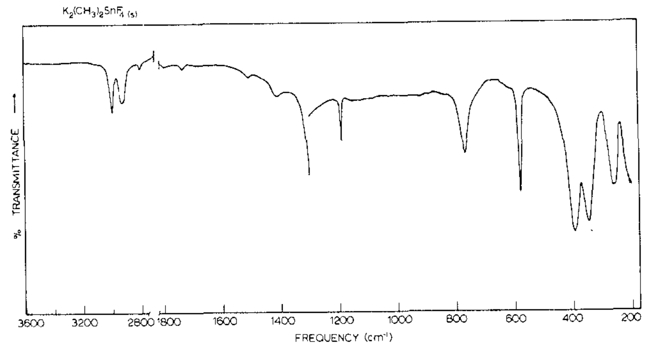

Figure 3.—Infrared spectrum of $K_2[(CH_3)_2SnF_4]$.

The Raman and infrared spectra of $K_2[(CH_3)_2SnF_4]$ which is obtained as a finely divided powder by dehydration of the dihydrate are illustrated in Figures 2 and 3. The infrared spectrum and the assignments for this compound differ somewhat from those in the literature.[11] The band reported previously at 553 cm^{-1} and assigned to Sn–C$_2$ asymmetric stretching was not observed in the anhydrous compound. In the 500–600-cm^{-1} region, only one intense band was observed at 582 cm^{-1} in the infrared spectrum, while the dihydrate $K_2[(CH_3)_2SnF_4]\cdot 2H_2O$ which was also examined showed two bands at 553 and 574 cm^{-1}. The Raman spectrum of the anhydrous material exhibited only one line in the Sn–C stretching region at 539 cm^{-1}. If the anhydrous compound is exposed to the atmosphere, an additional Raman line appears at 525 cm^{-1} and increases in intensity to the point where the 539-cm^{-1} line is only a shoulder. A hydrated single crystal was polished and sealed in a capillary with some of the mother liquor. Upon excitation of the Raman spectrum, only one intense band at 525 cm^{-1} was observed. When the crystal was exposed to the atmosphere, it effloresced, and the band at 539 cm^{-1} appeared. These effects are

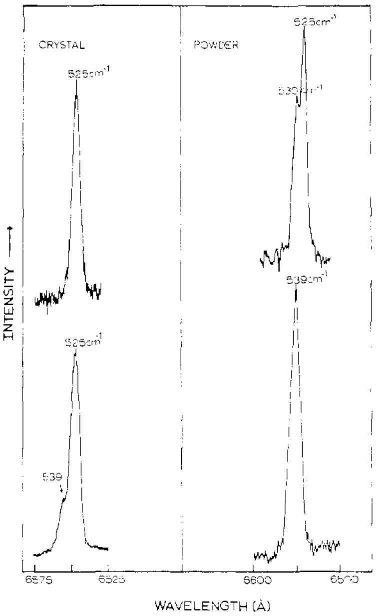

Figure 4.—Laser Raman spectra of $K_2[(CH_3)_2SnF_4]$ and $K_2[(CH_3)_2SnF_4]\cdot 2H_2O$ in the Sn–C stretching region: top left, single crystal of $K_2[(CH_3)_2SnF_4]\cdot 2H_2O$; bottom left, single crystal after efflorescence; bottom right, anhydrous $K_2[(CH_3)_2SnF_4]$ (powder); top right, powder after exposure to the atmosphere.

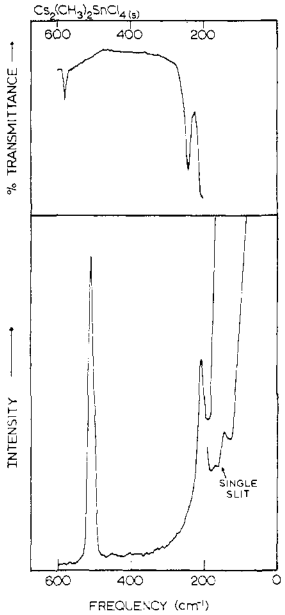

Figure 5.—Infrared and Hg arc excited Raman spectra of $Cs_2[(CH_3)_2SnCl_4]$ in the skeletal vibration region. The Raman bands at *ca.* 145 and 170 cm^{-1} are the characteristic grating ghosts of the Cary 81 spectrophotometer.

illustrated in Figure 4. We conclude that the band at 553 cm^{-1} assigned previously to asymmetric Sn–C stretching[11] for anhydrous $K_2[(CH_3)_2SnF_4]$ was caused by partial hydration of the crystals. The band assigned to Sn–F stretching previously must then be assigned to Sn–C stretching. The bands at 347 and 397 cm^{-1} are assigned to Sn–F stretching by analogy with $(CH_3)_2SnF_2$. The rather large splitting may result from Fermi resonance with a combination band; a comparable effect is observed with K_2PdCl_6.[25] A very

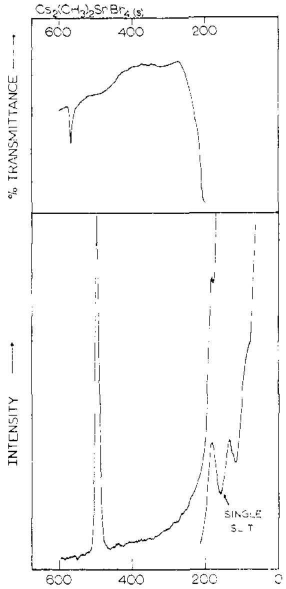

Figure 6.—Infrared and Hg arc excited Raman spectra of $Cs_2[(CH_3)_2SnBr_4]$ in the skeletal vibrational region. The signal at *ca.* 145 cm^{-1} is the grating ghost.

low intensity band at *ca.* 390 cm^{-1} was observed in the Raman spectrum of a single crystal of $K_2[(CH_3)_2SnF_4]\cdot 2H_2O$ which may be the totally symmetric Sn–F stretch. The band at 142 cm^{-1} probably involves C–Sn–F angle bending and would be analogous to the 140 cm^{-1} band of $(CH_3)_2SnF_2$ which has a very similar structure. The details of the assignment of the 224-cm^{-1} band in the Raman spectrum are not clear. The frequency is too low for Sn–F stretching. The Raman spectrum of crystalline K_2SnF_6 was examined, and only the totally symmetric stretch at *ca.* 590 cm^{-1} was a well-defined band with the anhydrous powder. Significant background scattering was observed below 400 cm^{-1}. With $SnCl_6^{2-}$, the relative Raman intensities for ν_1, ν_2, and ν_5 are *ca.* 10:1:3 with aqueous solutions and crystals. Consequently, considering the very low intensity of the totally symmetric Sn–F stretching vibration, it is very unlikely that the 224-cm^{-1} band involves F–Sn–F angle bending. This band is tentatively assigned to a lattice mode, *i.e.*, one not involving strictly internal vibrations of $(CH_3)_2SnF_4^{2-}$. Crystals of BaClF, BaBrF, and SrClF exhibit first-order Raman scattering with appreciable intensity in the 200–300-cm^{-1} range,[26] so assignment of this broad band to a lattice vibration involving fluoride is not unreasonable.

The Raman and infrared spectra of the chloro and bromo complexes are illustrated in Figures 2, 5, and 6. The assignments of the methyl and the Sn–C stretching frequencies are straightforward. Intense Raman and infrared bands are to be expected for Sn–Cl stretching at values lower than with $SnCl_6^{2-}$ (310 cm^{-1}, ν_1[27]) or R_2SnCl_2 (347 cm^{-1}, ν_s[28]). The bands at 207 and 197 in the Raman and 235 cm^{-1}

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[25] J. Hiraishi and T. Shimanouchi, *Spectrochim. Acta*, **22**, 1483 (1966).

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in the infrared are assigned to these vibrations. With the octahedral complexes $(CH_3)_2SnCl_2\cdot$phen and $(CH_3)_2SnCl_2\cdot$bipy (phen = 1,10-phenanthroline and bipy = α,α-bipyridyl), infrared-active Sn–Cl stretching is assigned in the range 239–247 cm^{-1}.[29]

Deformations involving primarily Cl–Sn–Cl binding, by analogy with related ions, *e.g.*, $SnCl_6^{2-}$ [27] and ICl_4^-,[30] would be expected to occur at *ca.* half the stretching frequency and consequently beyond the range of these measurements. Again a band is observed at *ca.* 140 cm^{-1}, and this is assigned to a skeletal deformation involving the C–Sn–Cl angle.

By analogy, the Sn–Br stretching vibrations would be expected to be below the values of R_2SnBr_2 compounds (240 ± 2 cm^{-1}, ν_s[28]) and of $SnBr_6^{2-}$ (184 cm^{-1}, ν_1[27]). With the octahedral complexes $(CH_3)_2SnBr_2\cdot$phen and $(CH_3)_2SnBr_2\cdot$bipy, these are assigned in the range 149–157 cm^{-1}.[29] A band is observed in the range of 170–185 cm^{-1} which has a contour very much like that assigned to the Raman-active Sn–Cl stretches. This was assigned to Sn–Br stretching. A band at 134 cm^{-1} was assigned to C–Sn–Br bending. Vibrations involving primarily Br–Sn–Br bending would be expected to occur below the range of the measurements. Grating ghosts complicate the assignments below 200 cm^{-1}, and spectra were obtained with two different spectrophotometers, one using an He–Ne laser and the other Hg arc excitation.

Because of the complex vibrations of the tetraethylammonium ion, it proved difficult to obtain a complete spectrum of the thiocyanate complex. Efforts to isolate this complex with an alkali metal ion were fruitless; indeed, all of these complexes are much more easily synthesized in pure form as salts of large organic cations. Fortunately, the $(C_2H_5)_4N^+$ ion did not interfere in the NCS deformation region, the tin–carbon stretching region, or the C≡N stretching region. The similarity of the tin–carbon stretching frequencies to those of the dimethyltin–aquo cation suggests that thiocyanate is bound by the nitrogen atom. The tin–proton coupling constants also are very similar to those of aqueous solutions of $(CH_3)_2Sn(ClO_4)_2$, $J(^{117}Sn\text{-}H)$ = 102.0, $J(^{119}Sn\text{-}H)$ = 107.0 Hz.[31] This structure also is supported by the thiocyanate deformation frequency, δ_{av} = 485 cm^{-1}. Frequencies in this region are quite characteristic of isothiocyanato complexes,[32] *cf.*, $\delta[Zn(NCS)_4^{2-}]$ = 482 cm^{-1}. Unfortunately, the weak C–S stretching frequency could not be observed because of interference by the cation. The spectrum of the $(CH_3)_2Sn(NCS)_4^{2-}$ anion cannot be interpreted in terms of an isolated ion with effective D_{4h} symmetry. There is a broad envelope of bands in the NCS deformation region, and in the C≡N stretching region there are two infrared-active and three Raman-active vibrations. For effective D_{4h} symmetry, there would be one infrared-active (e_u) and two Raman-active stretches (a_{1g} + b_{1g}). Because of the bulky cations present, this is more likely to be a consequence of low site symmetry rather than coupling within the unit cell. The values of the CN stretching frequencies also are consistent with[32] an isothiocyanate structure.

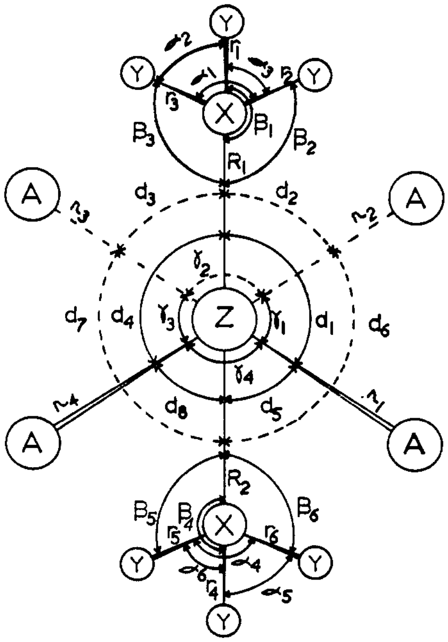

Figure 7.—Molecular model and internal coordinates for the $(CH_3)_2SnX_4^{2-}$ anions.

Because of the great lability of all of these complexes in solution which led to displacement of the halide or pseudohalide ligands, spectra only could be obtained on crystalline samples. Since detailed structures are not known for any of the compounds and in the case of the fluoro complex, at least, it is impossible to obtain macroscopic single crystals, certain limitations are inherent in the data.

Normal-Coordinate Analyses.—In order to study the effect of replacing two halides of the SnX_6^{2-} ions with two methide ligands, normal-coordinate calculations were carried out for the anions $(CH_3)_2SnX_4^{2-}$ (X^- = F^-, Cl^-, Br^-) using a Urey–Bradley force field (UBFF). For comparison, calculations were made with the UBFF for SnX_6^{2-} (X^- = F^-, Cl^-, Br^-). These hexahalogeno anions have been studied previously using the UBFF,[33] a modified Urey–Bradley force field (MUBFF),[34] and a simple valence force field (SVFF) plus four interaction constants.[27]

Figure 7 illustrates the molecular model for the *trans*-$(CH_3)_2SnX_4^{2-}$ ions and the 36 internal coordinates used to express the potential energy. In order to symmetrize the **F** and **G** matrices, the principle of local symmetry was employed.[35] The representation for the normal vibrations of a *trans*-ZA_2B_4 (D_{4h}) structure is Γ_{vib} = 2 A_{1g} + 2 A_{2u} + B_{1g} + B_{2g} + B_{2u} +

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$E_g + 3\ E_u$, and the 18 skeletal internal coordinates employed lead to redundancies in $A_{1g}(2)$ and B_{1g}. Considering the nondegenerate vibrations of the two CH_3 groups (z) and the degenerate vibrations (x, y) under the operations of D_{4h}, $\Gamma_{x,y,z} = \Gamma_z + \Gamma_{x,y}$; $\Gamma_z = A_{1g} + A_{2u}$ and $\Gamma_{x,y} = E_g + E_u$. In this way, the nine local symmetry coordinates, C_{3v} ($3\ A_1 + 3\ E$), for each of the two CH_3 groups were combined to yield 18 more symmetry coordinates involving the C–H bond lengths and the HCH and HCSn angles with redundancies in $A_{1g}(3)$, A_{2u}, and B_{1g}. Two torsional coordinates are ignored in this procedure. The justification for this is provided by neutron diffraction studies on $(CH_3)_2SnF_2$ which showed that the methyl groups were freely rotating at 23° and that the rotational barrier was probably less than a few tenths of 1 kcal.[36]

The potential energy was given by (1). The potential energy is independent of the conformation of the methyl groups.

$$\begin{aligned}2V = {} & \sum_{i=1}^{6}[2K'_{\mathrm{C-H}}r_{\mathrm{C-H}}(\Delta r^i_{\mathrm{C-H}}) + K_{\mathrm{C-H}}(\Delta r^i_{\mathrm{C-H}})^2] + \\ & \sum_{i=1}^{2}[2K'_{\mathrm{Sn-C}}R_{\mathrm{Sn-C}}(\Delta R^i_{\mathrm{Sn-C}}) + K_{\mathrm{Sn-C}}(\Delta R^i_{\mathrm{Sn-C}})^2] + \\ & \sum_{i=1}^{4}[2K'_{\mathrm{Sn-X}}r_{\mathrm{Sn-X}}(\Delta r^i_{\mathrm{Sn-X}}) + K_{\mathrm{Sn-X}}(\Delta r^i_{\mathrm{Sn-X}})^2] + \\ & \sum_{i=1}^{6}[2H'_{\mathrm{HCH}}(\Delta\alpha^i) + H_{\mathrm{HCH}}(\Delta\alpha^i)^2] + \sum_{i=1}^{6}[2H'_{\mathrm{HCSn}}(\Delta\beta^i) + \\ & H_{\mathrm{HCSn}}(\Delta\beta^i)^2] + \sum_{i=1}^{4}[2H'_{\mathrm{XSnX}}(\Delta\gamma^i) + H_{\mathrm{XSnX}}(\Delta\gamma^i)^2] + \\ & \sum_{i=1}^{8}[2H'_{\mathrm{CSnX}}(\Delta\delta^i) + H_{\mathrm{CSnX}}(\Delta\delta^i)^2] + \sum_{i=1}^{6}[2F'_{\mathrm{HH}}q_{\mathrm{HH}}(\Delta q^i_{\mathrm{HH}}) + \\ & F_{\mathrm{HH}}(\Delta q^i_{\mathrm{HH}})^2] + \sum_{i=1}^{6}[2F'_{\mathrm{HSn}}q_{\mathrm{HSn}}(\Delta q^i_{\mathrm{HSn}}) + F_{\mathrm{HSn}}(\Delta q^i_{\mathrm{HSn}})^2] + \\ & \sum_{i=1}^{8}[2F'_{\mathrm{CX}}q_{\mathrm{CX}}(\Delta q^i_{\mathrm{CX}}) + F_{\mathrm{CX}}(\Delta q^i_{\mathrm{CX}})^2] + \\ & \sum_{i=1}^{4}[2F'_{\mathrm{XX}}q_{\mathrm{XX}}(\Delta q^i_{\mathrm{XX}}) + F_{\mathrm{XX}}(\Delta q^i_{\mathrm{XX}})^2] \qquad (1)\end{aligned}$$

Force constants were calculated by the same procedures used in earlier papers in this series.[21,37] Trial values were adjusted to minimize the sum of the squares of the residuals in the frequency parameters.[38] Weights were taken proportional to $1/\lambda$, and the calculations were carried out using the University of Minnesota's CDC-6600 and Purdue University's CDC-6500 computers. Geometrical parameters[39–43] used in the calculations are given in Table III.

TABLE III
MOLECULAR PARAMETERS[a]

Bond	Length, Å	Bond	Length, Å
Sn–F	2.00[39]	Sn–C	2.08[42]
Sn–Cl	2.41[40]	C–H	1.093[43]
Sn–Br	2.59[41]		

[a] ∠H–C–H = ∠H–C–Sn = 109° 28′; ∠C–Sn–X = ∠X–Sn–X = 90°.

Calculations were made in a similar manner for the octahedral SnX_6^{2-} anions. Trial values of the force constants were taken from the calculation of Hiraishi, *et al.*[33] The force constants from the last cycle of the least-squares refinements for the SnX_6^{2-} ions are listed in Table IV, and the calculated and observed frequencies[33,44–48] are tabulated in Table V. The force constants differ slightly from the earlier UBFF values, because more frequencies were available and because least-squares refinement was employed.

TABLE IV
UB AND VALENCE FORCE CONSTANTS[a] WITH
STANDARD ERRORS FOR SnX_6^{2-} IONS

	SnF_6^{2-}		$SnCl_6^{2-}$		$SnBr_6^{2-}$	
Description	UB	F_{dia}	UB	F_{dia}	UB	F_{dia}
K(Sn–X)	2.30 (0.35)	2.80	1.09 (0.15)	1.46	0.84 (0.02)	1.18
H(X–Sn–X)	0.18 (0.45)	0.79	0.26 (0.30)	0.91	0.01 (0.05)	0.70
F(X···X)	0.28 (0.21)	...	0.20 (0.11)	...	0.19 (0.02)	...

[a] K and F in mdyn/Å; H in mdyn Å/radian²; standard errors from least-squares refinement in parentheses.

TABLE V
OBSERVED AND CALCULATED FREQUENCIES
(CM⁻¹) FOR SnX_6^{2-} IN A UBFF[a]

	SnF_6^{2-}		$SnCl_6^{2-}$		$SnBr_6^{2-}$	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
A_{1g}	578	553	312	302	184	184
E_g	465	473	233	243	141	144
F_{2g}	244	266	161	173	95	94
F_{1u}	555	557	317	313	217	216
	256	223	174	159	95	96
F_{2u}	...	188	...	122	...	67
Av error	6.54%		5.30%		0.97%	

[a] The observed frequencies are average values of data in the literature: SnF_6^{2-}, ref 44; $SnCl_6^{2-}$, ref 33, 45–48; $SnBr_6^{2-}$, ref 33, 46–48.

The UBFF provides a fair description of the forces operating in SnF_6^{2-} and $SnCl_6^{2-}$ and a very much better representation for $SnBr_6^{2-}$. The addition of *trans* stretch–stretch interactions and interactions between adjacent noncoplanar angles improves the fit but requires the determination of as many force constants as available frequency values. Since the completion of this work, a GVFF with five variable parameters has been used in calculations on these ions.[27] The valence force constants of Wharf and Shriver—2.900, 1.435, and 1.200 for SnF_6^{2-}, $SnCl_6^{2-}$, and $SnBr_6^{2-}$, respectively—may be compared with the diagonal elements of the **F** matrix from this work with the UBFF, 2.80, 1.46, and 1.18 mdyn/Å. The UBFF yields reasonably accurate values for the stretching force con-

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TABLE VI
UB AND VALENCE FORCE CONSTANTS[a] WITH STANDARD ERRORS FOR $(CH_3)_2SnX_4^{2-}$ IONS

	$(CH_3)_2SnF_4^{2-}$		$(CH_3)_2SnCl_4^{2-}$		$(CH_3)_2SnBr_4^{2-}$	
	UB	Valence	UB	Valence	UB	Valence
K(C–H)	4.63 (0.02)	4.86 (0.02)	4.71 (0.02)	4.91 (0.02)	4.69 (0.02)	4.90 (0.02)
K(C–Sn)	1.53 (0.06)	2.54 (0.06)	1.29 (0.07)	2.44 (0.07)	1.23 (0.12)	2.37 (0.12)
K(Sn–X)	0.99 (0.04)	1.24 (0.04)	0.66 (0.06)	0.81 (0.07)	0.71 (0.14)	1.07 (0.17)
H(H–C–H)	0.48 (0.008)	0.51 (0.009)	0.49 (0.01)	0.51 (0.01)	0.48 (0.01)	0.49 (0.02)
H(H–C–Sn)	0.10 (0.006)	0.42 (0.006)	0.11 (0.01)	0.43 (0.01)	0.11 (0.01)	0.43 (0.01)
H(X–Sn–X)	0.60 (0.06)	1.22 (0.06)	0.12[b]	0.30	0.005[b]	1.02
H(C–Sn–X)	0.21 (0.02)	0.22 (0.02)	0.04 (0.04)	0.31 (0.04)	0.05 (0.08)	0.34 (0.08)
F(X···X)	0.28[b]		0.05 (0.06)		0.28 (0.22)	
F(C···X)	0.005[b]		0.10[b]		0.10[b]	
F(H···Sn)[b]	0.40[b]		0.40[b]		0.40[b]	
F(H···H)	0.06 (0.01)		0.03 (0.02)		0.04 (0.03)	
κ[b]	0.00[b]		0.00[b]		0.00[b]	

[a] K and F in mdyn/Å; H and κ in mdyn Å/radian;[2] valence force constants obtained by transformation from the UBFF. [b] Constrained.

stants. Since the calculations on the $(CH_3)_2SnX_4^{2-}$ anions require a simple model force field, only the UBFF was used for the SnX_6^{2-} ions.

In the calculations for the $(CH_3)_2SnX_4^{2-}$ ions, the starting values for K_{Sn-C}, K_{C-H}, H_{HCH}, H_{HCSn}, F_{HH}, and F_{HSn} were taken from the calculation on $(CH_3)_2Sn(aq)^{2+}$.[37] The trial values for K_{SnX} and H_{XSnX} were taken as 50% of the values for the corresponding SnX_6^{2-} ions. Values for the nonbonded interaction constants were estimated from Lennard-Jones potentials.[49] The force fields are similar to those employed in studies on halogenoammine complexes of transition metals.[50] The force constants from the last cycle of least-squares refinement are listed in Table VI, and the calculated and observed frequencies are compared in Table VII.

TABLE VII
OBSERVED AND CALCULATED FREQUENCIES
(CM^{-1}) FOR $(CH_3)_2SnX_4^{2-}$

	ν, cm^{-1}						
	$K_2[(CH_3)_2SnF_4]$		$Cs_2[(CH_3)_2SnCl_4]$		$Cs_2[(CH_3)_2SnBr_4]$		Principal contribution
Mode	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	
A_{1g}	2916	2921	2926	2927	2918	2924	ν(C–H)
	1214	1205	1203	1209	1194	1200	δ(H–C–H)
	539	528	508	516	498	507	ν(C–Sn)
	...	372	207	203	183	170	ν(Sn–X)
A_{2u}	2926	2921	2930	2927	2930	2924	ν(C–H)
	1195	1206	1192	1210	1193	1201	δ(H–C–H)
	582	591	580	571	571	562	ν(Sn–C)
	...	122	...	98	...	81	δ(X–Sn–X)
B_{1g}	...	289	197	190	174	128	ν(Sn–X)
E_g	2998	3000	3023	3022	3017	3016	ν(C–H)
	...	1409	...	1404	1380	1388	δ(H–C–H)
	...	769	...	781	...	780	ρ(H–C–Sn)
	142	142	139	139	134	134	δ(C–Sn–X)
E_u	3001	3000	3020	3022	3015	3016	ν(C–H)
	1410	1409	1410	1404	1400	1388	δ(H–C–H)
	773	772	793	783	788	783	ρ(H–C–Sn)
	372[a]	372	235	238	...	202	ν(Sn–X)
	...	109	...	127	...	133	δ(C–Sn–X)
	257	257	...	80	...	96	δ(X–Sn–X)
Av error	0.3%		0.9%		3.0%		

[a] Average of 347 + 397 cm^{-1}.

Because of the limited frequency data (only 13–14 frequencies were observed experimentally), only eight force constants were refined and four were constrained. Calculated frequencies for the $B_{2g}(1)$ and $B_{2u}(1)$ modes which involve low-frequency bending vibrations for which no experimental values were available are not reported in Table VII. Because of the paucity of data for the bending vibrations and lattice effects, *no physical significance should be placed on the values of the skeletal bending force constants.* Some of the problems involved in analogous calculations on large coordination compounds and the significance of the force constants are discussed elsewhere.[21]

Discussion

To a first approximation, the crystal structure of $(CH_3)_2SnF_2$ may be regarded as basically an ionic one with linear $(CH_3)_2Sn^{2+}$ cations and F^- anions held together by hard-sphere coulombic interactions,[4,51] a description which is rather different from that given by Clark and Goel.[23] The vibrational spectra are in accord with this model, and the very low Raman intensity of the Sn–F stretching vibrations confirms the highly ionic nature of the Sn–F interactions. The Raman spectrum of $(CH_3)_2SnF_2$ is virtually identical with that of $(CH_3)_2Sn^{2+}$ recorded with an aqueous solution, and both spectra are typical of a nine-atom $(CH_3)_2Sn^{2+}$ cation.

The Raman and infrared spectra of the $(CH_3)_2SnX_4^{2-}$ anions ($X^- = F^-, Cl^-, Br^-, NCS^-$) are only in accord with the *trans* structure for these anions which has been assigned previously on the basis of infrared spectra alone.

The normal-coordinate analysis is most satisfactory for $Cs_2[(CH_3)_2SnCl_4]$ where the frequency data were most complete. With the fairly strong bonds within the complex anion and the large cesium cation, coupling with lattice modes should not influence appreciably the values obtained for the stretching force constants. Because the spectra of $K_2[(CH_3)_2SnF_4]$ indicate quite weak tin–fluoride interactions (the highest infrared-active stretching frequency is only 397 cm^{-1} compared to 555 cm^{-1} for SnF_6^{2-}), the treatment in terms of a free $(CH_3)_2SnF_4^{2-}$ anion is probably less satisfactory. Coupling with lattice modes may well be significant here, and certain features of the spectra suggest this. The unusually high F–Sn–F

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(51) See, for example, the discussion by R. S. Tobias, *Organometal Chem. Rev.*, **1**, 93 (1966).

bending force constant obtained also suggests that the deformation is not that of a free $(CH_3)_2SnF_4^{2-}$ anion. Since it proved impossible to isolate a pure complex with Cs^+ in place of K^+ and the synthesis of the potassium salt with the correct stoichiometry took considerable effort, the potassium ions may be important in stabilizing the structure. The fit to the tin–halogen stretching frequencies is less satisfactory for $Cs_2[(CH_3)_2SnBr_4]$ than for $Cs_2[(CH_3)_2SnCl_4]$. Although the infrared-active Sn–Br stretch was not observed, it cannot be higher than *ca.* 220 cm^{-1}. This constraint was applied in the calculation together with the assignment of the shoulder at 174 cm^{-1} as the B_{1g} Sn–Br stretch. The frequency pattern is similar to that observed for ICl_4^-,[30] for which the Urey–Bradley field is rather bad. In order to obtain a good description of the ICl_4^- force field, it is necessary to use a GVFF with a rather large *trans* stretch–stretch interaction.[30] There also may be some coupling of the vibrations of different anions within the unit cell, for the X-ray measurements showed that $Cs_2[(CH_3)_2SnBr_4]$ contains four formula units per cell. This would be expected to affect particularly the Br–Sn–Br deformations and, to a lesser extent, the Sn–Br stretches. The orthorhombic cell was somewhat of a surprise, for it was thought that the unit cell would reflect the symmetry of the anion and be tetragonal.

Since the Urey–Bradley nonbonded force constants make appreciable contributions in the potential energy distribution for the stretching frequencies, it is simpler to use the diagonal elements of the **F** matrix expressed in internal coordinates, *i.e.*, the valence force constants, to discuss trends in bond strengths.

The decrease in the skeletal frequencies assigned to $Sn-C_2$ stretching and the Sn–C stretching force constants suggests that there is increasing covalency in the tin–halogen interactions from F^- to Br^-. None of the valence Sn–C force constants was affected significantly by large changes in the bending force constants. For example, if H(C–Sn–X) is constrained at 0, the largest change in any of the constants is 0.02 mdyn/Å. This effect on the tin–carbon bonds caused by changing the halide ion is considerably smaller than that observed in going from $[Hg(NH_3)_2]Cl_2$ to $[Hg(NH_3)_2]Br$.[32] In these compounds, the linear diamminemercury(II) ion is surrounded by four halide ions in the equatorial plane. In the ionic $(CH_3)_2TlX$ compounds, the corresponding decrease in $\nu_s(Tl-C_2)$ in going from X = Cl to Br is only 5 cm^{-1}.[37] The valence force constant for Sn–C stretching for the aquo cation is 2.51 mdyn/Å[37] which is intermediate between that of $(CH_3)_2SnF_4^{2-}$ and $(CH_3)_2SnCl_4^{2-}$ but not significantly different from either.

The spectra of the thiocyanato complex suggest that the coordination is *via* nitrogen which is reasonable since the tin–carbon stretching frequencies are almost the same as for the aquo ion. Also the indirect tin–proton coupling constants for the complex thiocyanate anion measured with an acetone solution, $J(^{117}Sn-H) = 108$, $J(^{119}Sn-H) = 113$ Hz, are similar to the values for the aquo cation, 102 and 106 Hz, respectively.

There is a large decrease in the Sn–X stretching force constant as two fluorides are replaced by two methyl groups, a smaller but still significant decrease with the chloro complex, and little change with the bromo complex. This trend parallels the increase in tin–halogen covalency suggested by the Sn–C stretching frequencies and force constants. The effect is very similar to that observed with transition metal complexes, *e.g.*, Au(III),[21] as ligands like CH_3^- replace halide ions. With the transition elements, the bond weakening occurs *trans* to the alkyl group, while with the tin complexes it is directed to the *cis* positions. The Sn–Cl valence stretching force constant of $(CH_3)_2SnCl_4^{2-}$ is appreciably smaller than the I–Cl stretching force constant of the stereochemically related square-planar ICl_4^-, 1.27 mdyn/Å.[30] This is to be expected because of the increase in nuclear charge from tin to iodine.

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