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# STUDIES ON ADDUCTS OF ORGANOTIN(IV) HALIDES WITH BIS(ACETYLACETONE)ETHYLENEDIIMINE

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## SUMMARY

The solid state configuration of 1/1 adducts, formed by mono-, di- and triorganotin(IV) halides with the potentially tetradentate ligand bis(acetylacetone)ethylenediimine, has been investigated. The infrared spectra suggest that the neutral ligand coordinates $Sn^{IV}$ through N (or O) atoms of the H-bonded acetylacetoneimine moieties. The skeletal vibrations associated to Sn–C and Sn–Cl bonds are consistent with square planar configurations of the organotin(IV) halide moieties, where $SnCl_3$ and $C_3Sn$ groups would be T-shaped, and $Alk_2SnCl_2$ would have *trans*-dialkyl, *trans*-dichloro arrangements. The latter configuration is supported by the magnitude of the quadrupole splittings. Measurements of the temperature dependence of the Debye–Waller factor, as obtained by Mössbauer spectroscopy for the $(CH_3)_3SnCl$ adduct, indicate a polymeric structure. An octahedral type configuration is then proposed. in which the planar organotin(IV) halide moieties are bridged by the ligand, axially coordinating tin(IV).

## INTRODUCTION

Earlier studies have demonstrated the tendency of potentially tetradentate bases (formed by condensation of ethylenediamine or 1,2-diaminopropane with acetylacetone) to act as neutral ligands, rather than as dianion coordinating agents, towards several organothallium(III), organolead(IV) and organotin(IV) halides[1,2]. Complexes such as $R_2SnCl_2 \cdot L$ (R = Me and Ph, L = tetradentate base), *inter alia*, have been prepared[1,2]. The present paper deals with a thorough investigation of solid organotin(IV) halide–tetradentate ligand adducts. The ligand bis(acetylacetone)ethylenediimine (= Acen), which is assumed to have a structure corresponding to 4,4'-(ethylenediimino)di(3-penten-2-one)[3], was selected for detailed study. New 1/1 adducts of Acen with $CH_3SnCl_3$, $(CH_3)_2SnBr_2$, $(CH_3)_3SnCl$, $(n\text{-}C_4H_9)_2SnCl_2$ were prepared, and the configuration of the series was investigated in the solid state by infrared and Mössbauer spectroscopies.

## EXPERIMENTAL

The organotin compounds used for syntheses were obtained from Fluka and Alfa Inorganics. The other reagents and solvents were of analytical grade, and, where appropriate, were purified by standard procedures.

The ligand Acen was prepared and recrystallized according to literature methods[4,5].

The complexes $R_2SnCl_2$Acen (R = Me and Ph) were obtained as reported earlier[1,2]. $Me_2SnCl_2$Acen melted with decomposition at 184–186° (lit.[1,2] 158–160°).

The Acen derivatives of $MeSnCl_3$, $Me_2SnBr_2$, $Me_3SnCl$, and $Bu_2SnCl_2$ were prepared by adding 3 mmole of the organometal halide in 10–30 ml of n-hexane (b.p. 65–68°) dropwise and with stirring to a boiling solution containing 3 mmole of Acen in 200 ml of n-hexane. (Warming was necessary to dissolve $Me_2SnBr_2$). The compound $MeSnCl_3 \cdot$Acen precipated immediately as a white gelatinous solid, which became crystalline on boiling when the addition of $MeSnCl_3$ was completed. Immediate precipitation takes place also with $Me_2SnBr_2$Acen, to give a white microcrystalline solid. The compounds $Me_3SnCl$Acen and $Bu_2SnCl_2$Acen slowly crystallized on cooling as white needles and star-like needles, respectively. The solids were recovered by filtration, washed with n-hexane, and dried under vacuum. The yields were nearly 100%. The derivatives of $Me_3SnCl$ and $Bu_2SnCl_2$ are much more soluble in donor solvents (*e.g.* acetone) than those of $MeSnCl_3$, $Me_2SnBr_2$ and $R_2SnCl_2$. The melting points and analytical data are reported in Table 1.

TABLE 1

ANALYTICAL DATA

| Compound | M.p. (°C) | Elemental analysis, found (calcd.) (%) | | | | |
|---|---|---|---|---|---|---|
| | | C | H | N | Halogen | Sn |
| $MeSnCl_3$Acen | 151–152<br>Dec. | 33.82<br>(33.62) | 5.05<br>(4.99) | 5.96<br>(6.03) | 22.99<br>(22.90) | 25.50<br>(25.56) |
| $Me_2SnBr_2$Acen | 182–185<br>Dec. | 31.55<br>(31.55) | 4.93<br>(4.92) | 5.33<br>(5.26) | 30.05<br>(29.99) | 22.14<br>(22.27) |
| $Me_3SnCl$Acen | 94–97 | 42.90<br>(42.54) | 6.31<br>(6.90) | 6.82<br>(6.61) | 8.26<br>(8.37) | [a] |
| $Bu_2SnCl_2$Acen | 112 | 45.35<br>(45.49) | 7.38<br>(7.25) | 5.20<br>(5.31) | 13.67<br>(13.43) | 22.21<br>(22.48) |

[a] Not determined (as $SnO_2$) owing to the volatility of the adduct.

Infrared spectra were taken with Perkin–Elmer 457 and 621 instruments, calibrated with polystyrene films, on nujol and hexachlorobutadiene mulls, using CsI windows, in the range 4000–200 $cm^{-1}$. Results are reported below for all compounds except Acen (for which only the 400–200 $\bar{\nu}$ spectrum is shown) and $Me_2SnBr_2$Acen (reported in the 4000–250 $\bar{\nu}$ range), and are believed to be accurate within $\pm 3\ cm^{-1}$ for the $\bar{\nu}$ range 2000–200, and within $\pm 10\ cm^{-1}$ for 4000–2000 $\bar{\nu}$. The spectrum of free Acen was found to correspond to previously reported data[6,7] in the $\bar{\nu}$ range 4000–400. Starred values refer to hexachlorobutadiene mulls. s, strong; v, very; m, medium; w, weak; bd, broad; sh, shoulder.

(1). *Acen*

385 w; 345 w; 200 w.

(2). $MeSnCl_3Acen$

3200* sh; 3140* m, bd; 3000* w; 2950* sh; 2920* sh; 1610 s; 1545 vs; 1485* s; 1440* s; 1380* vs; 1360 sh; 1325 s; 1280 s, bd; 1210 s; 1140 m; 1095 m; 1025 m; 995 m; 945 s; 845 w; 830 m; 800 s; 790 s; 765 m; 720 vw; 650 vw–554 vw; 537 w; 527 w; 423 vs; 383 vvw; 310 m; 282 vs; 261 vs; 235 sh; 204 m.

(3). $Me_2SnCl_2Acen$

3160* m, bd; 2990* vw; 2950* vw; 2920* vw; 1595 s; 1545 sh; 1535 s; 1495* sh; 1465* w; 1430* m; 1370* m; 1340 s; 1285 s; 1210 s; 1096 m; 1020 m; 995 m; 950 m; 855 sh; 835–780 m, bd; 760 s; 720 sh; 650 vw–586 w; 550 vvw; 423 vs; 365 vw; 345 vw; 238 s.

(4). $Me_2SnBr_2Acen$

3160* m, bd; 2990* vw; 2950* vw; 2920* vw; 1595 vs; 1545 sh; 1535 vs; 1495* s; 1460* sh; 1430* m; 1370* w; 1340 vs; 1305 sh; 1285 vs; 1210 s; 1090 m; 1025 m; 995 m; 950 s; 855 w; 825–795 m, bd; 760 s; 720 w; 650 vw; 575 w; 535 vw; 415 s; 280 vw.

(5). $Me_3SnClAcen$

3180* m,bd; 3000*–2920* s,bd (component bands at 3000, 2980, 2950, 2920) 1700–1480 s,bd; 1470* vw; 1440* s; 1370* sh; 1365* s; 1330 s; 1280 vs,bd; 1220 s; 1205 sh; 1180 w; 1140 w; 1095 m; 1025 m; 975 m; 940 m; 850 m; 830 sh; 775 vs,bd; 735 m; 650 w; 640 w–558 s; 526 m; 413 m,bd; 370 w; 265 s.

(6). $Bu_2SnCl_2Acen$

3160* m,bd; 2960* m; 2920* m; 2850* m; 1600 vs; 1550 sh; 1535 vs; 1500*–1400* vs,bd (component bands at 1500, 1460, 1440); 1365* m; 1340 s; 1280 s,bd; 1210 s; 1155 w; 1100 s; 1025 m; 990 m; 950 s; 850 m; 830 m; 765 s; 720 w; 690 m; 650 w; 630 vw–550 vvw; 420 vs; 365 vw; 342 vw; 220 vs,bd.

(7). $Ph_2SnCl_2Acen$

3200*–2800* m,bd; 3080*–2880* m,bd (component bands at 3080, 3060, 3000, 2950, 2880); 1610–1500 vs,bd (component bands at 1610, 1590, 1545, 1500); 1480* m; 1430* s; 1380* w; 1360* m; 1330 s; 1300 sh; 1285 vs; 1225 w; 1205 w; 1185 w; 1135 vw; 1110 m; 1070 w; 1020 m; 995 m; 940 m; 850 vw; 815 w; 775 w; 760 m; 740 s; 730 s; 695 s; 690 s; 650 vw–547 w; 500 w; 464 s; 427 s; 393 vvw; 377 vvw; 335 vvw; 290 sh; 275 s; 237 s.

Mössbauer spectra were obtained using a constant acceleration transducer in conjunction with an 800 channel multichannel analyzer operated in the multiscaler mode. The samples were mounted in copper sample holders as layers of microcrystalline material covered with 0.5 mm aluminum foil as a thermal shield. In the constant temperature experiments, sample temperatures were held to 81 ± 2°K using a calibrated thermocouple. Temperature dependence data on the recoil-free fraction were obtained using a variable temperature Dewar (Hoffman–Andonian) in con-

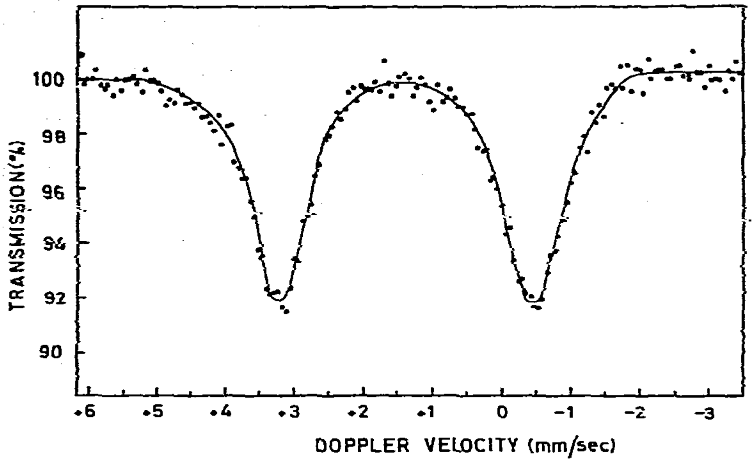

Fig. 1. The Mössbauer spectrum of $Ph_2SnCl_2$Acen at 80°K.

TABLE 2

MÖSSBAUER PARAMETERS FOR THE OCTAHEDRAL ORGANOTIN(IV) HALIDE–Acen ADDUCTS DISCUSSED IN THE TEXT[a]

| Compound | *IS*[b] (mm/sec) | *QS* (mm/sec) | T (°K) | $\log_{10}A$[c] | $\log_{10}A/A_{120}$[c] |
|---|---|---|---|---|---|
| $MeSnCl_3$Acen | 0.91 | 2.25 | 83 | | |
| $Me_2SnCl_2$Acen | 1.46 | 4.33 | 79 | | |
| $Me_2SnBr_2$Acen | 1.53 | 4.34 | 80 | | |
| $Ph_2SnCl_2$Acen | 1.34 | 3.62 | 80 | | |
| $Bu_2SnCl_2$Acen | 1.64 | 4.40 | 82 | | |
| $Me_3SnCl$Acen[d] | 1.38 | 3.49 | 79 | 2.458 | 1.138 |
| | | | 150 | 1.945 | 0.901 |
| | | | 200 | 1.530 | 0.708 |
| | | | 240 | 1.231 | 0.570 |

[a] Linewidths at half-heigths, $\Gamma^+$ and $\Gamma^-$, range between 1.19 and 0.90 mm/sec. [b] With respect to the centroid of a $BaSnO_3$–$BaSnO_3$ spectrum at 294°K. [c] The resonance absorption area, *A*, normalized to the area at 120°K, $A_{120}$. [d] No effect observable at 294°K.

junction with calibrated resistance thermometers. Spectrometer calibration was effected using a Pd($^{57}$Co) source in conjunction with an N.B.S. standard 0.8 mil 99.99% pure iron foil and the ground state splitting value[8] 3.9177 mm/sec at 24°. The zero of motion was determined from a room temperature $BaSnO_3$–$BaSnO_3$ spectrum*, and all isomer shifts are reported with respect to the center of this spectrum.

Data reduction of the Mössbauer results was effected by standard computations. The resonance lines were assumed to be Lorentzian and line position, effect magnitude and line width were allowed to vary as independent parameters. Corrections for nonlinearity in the base line were made as needed.

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* Such data are directly comparable to isomer shifts reported with respect to $SnO_2$ within the experimental error quoted.

The results are reported in Table 2. A typical Mössbauer spectrum is shown in Fig. 1.

## DISCUSSION

Inspection of the data in Table 1 clearly shows that Acen acts as a neutral donor molecule towards organotin(IV) halides, irrespective of the number and nature of the organic moieties bound to tin(IV). This is consistent with the acceptor properties of tin(IV) derivatives as well as with some aspects of the coordinating behaviour of the Acen ligand. In fact, tin(IV) tetrahalides form a variety of adducts with neutral donors[9,10] (including acetylacetone[11], two half-molecules of which may be considered to exist in one molecule of Acen), as has also been observed for a variety of organotin(IV) derivatives[12]. Moreover, subsequent to our studies of organometallic adducts[1], it has been reported that neutral Acen coordinates lanthanide salts[13] as well as $ZnCl_2$[14].

The nature of the ligand-to-organometal bonds and the configuration of the adducts will be discussed below for these solids on the basis of the available infrared and Mössbauer spectral data.

The infrared spectra of free and coordinated Acen do not substantially differ in the 3000 cm$^{-1}$ region. The bands of the adducts centered at about 3200–3140 cm$^{-1}$ correspond to the broad band of Acen around 3150 cm$^{-1}$ probably due to H-bonded $\nu$(OH) or $\nu$(NH)[6,7], which would imply that the coordinated ligand maintains the N–H–O bonding in its acetylacetoneimine moieties. This is further supported by the appearance of the very strong band at 1280–1285 cm$^{-1}$ in all the spectra of the adducts, fully corresponding to the 1286 cm$^{-1}$ band of free Acen, which is believed to arise from O–H deformation vibrations in the H-bonded rings[6]. In this context the hypothesis that Acen coordinates the organotins as a tetradentate neutral base[2], in the diketo dinitrilo form, or in other forms[13], seems to be unlikely.

The strong broad bands of coordinated Acen in the 1610–1485 cm$^{-1}$ region differ in the individual adducts and in free Acen. These were assigned to $\nu$(C=O), $\nu$(C=C) and $\nu$(C=N) in Acen H-bonded rings[6,7]. It may be inferred that changes in the bonding occurred upon coordination, suggesting that the oxygen and nitrogen ring atoms, having electronic lone pairs, could be involved in bond formation with tin(IV).

The spectra of Acen and its organotin(IV) halide adducts are essentially identical in the 1480–600 cm$^{-1}$ range, if allowance is made for the vibrations involving the organic moieties bound to tin(IV)[15-18].

The strong, sharp bands around 420 cm$^{-1}$ (medium broad for $Me_3SnClAcen$) are common to all adducts. They cannot be attributed to a ligand vibration[6], nor to the skeletal fundamentals of the organotin halides (the latter are located at different energies). The 420 cm$^{-1}$ band is then assigned to a tin–ligand atom vibration, *i.e.*, Sn–O or Sn–N. An unambiguous assignment to Sn–O or Sn–N vibrational modes is not feasible on the basis of literature data, since energies associated with the two types of bonds are spread out over a wide range[18-20]. In any event, since no other bands attributable to tin–ligand vibrations were detected in the low energy region which has been examined, the sharpness and intensity of the 420 cm$^{-1}$ band suggest that only one of the two possible tin–ligand atom bonds occurs; moreover, if two basic atoms of one Acen molecule coordinate organometallic moieties, it is reasonable to conclude that they occupy *trans* positions with respect to the metal atom. On this basis, it is assumed that the 420 $cm^{-1}$ band is due to a Sn–N vibration, as suggested by the comparison of the spectra of the Acen adducts with those of the complexes $R_2SnSalen$[21]. The latter are believed to contain two Sn–O and two Sn–N bonds in a square plane, and show two bands attributable to tin–ligand atom vibrations around 600 and 400 $cm^{-1}$ [21]. The N atoms coordinating tin(IV) in the Salen complexes and Acen adducts are expected to be of the same type, *i.e.*, nitrogen from the ethylenediamine fragment. It is then reasonable to tentatively attribute the bands around 400 $cm^{-1}$ to Sn–N vibrations for the two series of compounds.

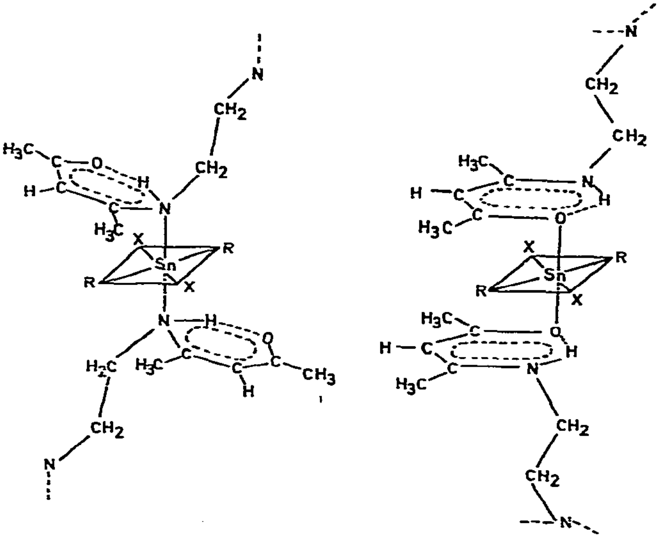
In order to elucidate the nature of the adducts, the tin–halogen frequencies, which should occur at low energies, must be considered. A further coordination on the tin(IV) atom decreases $\nu$(Sn–Cl)[22], as expected by the increase of the electronic charge located on the tin atom, which would give rise to an increase of the per cent ionic character of the tin–halogen bonds. We attribute to Sn–Cl vibrations the following bands: (a) $MeSnCl_3Acen$: 310, 282 and 261 $cm^{-1}$; (b) $Me_2SnCl_2Acen$ and (perhaps) $Ph_2SnCl_2$ Acen: 238–237 $cm^{-1}$ (in the spectrum of the diphenyl derivative, a Sn–Ph vibration occurs at the same frequency)[23]; (c) $Me_3SnClAcen$: 265 $cm^{-1}$; (d) $Bu_2SnCl_2Acen$: 220 $cm^{-1}$. Tin–halogen frequencies for $Me_2SnBr_2Acen$ probably lie below 250 $cm^{-1}$, and were not observed. A similar drastic diminution of the tin–halogen frequencies from the uncoordinated compounds[15–17,22–24] to their adducts was detected in a number of cases[25–28].

The occurrence of three or more Sn–Cl bands for $MeSnCl_3Acen$ indicates a decrease of the symmetry for the $SnCl_3$ group, which shows two stretching modes in $MeSnCl_3$, solution phase, according to the predictions based on $C_{3v}$ symmetry[16]. A corresponding result was reported for $\nu$(SnCl) in [$Me_4N$] [$Me_2SnCl_3$] and similar compounds[26], where the $SnCl_3$ group is T-shaped[29]. The same configuration could then be tentatively assumed for $SnCl_3$ in $MeSnCl_3Acen$.

Symmetrical and antisymmetrical $\nu(SnCl_2)$ occur in $Me_2SnCl_2$, which is thought to belong to the $C_{2v}$ point group[16]. A multiplicity of $\nu(SnCl_2)$ bands is observed for six-coordinated diorganotin(IV) dihalide adducts where the two halide atoms are believed to lie in *cis*-position[26,28]. The strong, single band detected at 238 $cm^{-1}$ for $Me_2SnCl_2Acen$, being the only one in the low energy spectrum attributable to $\nu(SnCl_2)$, would suggest a linear ClSnCl group. The same structure could be advanced for the metal–halide group in $Bu_2SnCl_2Acen$.

Vibrations associated with Sn–C skeletal modes[17,23–25] could not be identified in $Bu_2SnCl_2Acen$; these modes are found to occur at 464, 275 and 237 $cm^{-1}$ in $Ph_2SnCl_2Acen$, and 537 or 527 $cm^{-1}$ in $MeSnCl_3Acen$. The weak or very weak bands occurring around 550–535 $cm^{-1}$ in all adducts are most probably ligand vibrations, based on a thorough comparison of free and coordinated Acen spectra. On this basis, the bands at 586 and 575 $cm^{-1}$ of the two compounds $Me_2Snhal_2Acen$ are assigned to $\nu_{as}(SnC_2)$ and no evidence for $\nu_{sym}(SnC_2)$[15,16] is found. This implies that linear CSnC groups[12,25,26] are present in both adducts. The two bands observed at 558 and 526 $cm^{-1}$ in $Me_3SnClAcen$ seem to be associated with Sn–C vibrations. In fact, the 545 and 514 $cm^{-1}$ bands observed for liquid $Me_3SnCl$, point group $C_{3v}$, were assigned to $\nu(SnC_3)$[15,16]. The latter symmetry is unlikely for the $SnC_3$ group in $Me_3SnClAcen$. On the other hand, two bands could be expected for a T-shaped configuration, one arising from $\nu_{as}(SnC_2)$ of the linear CSnC moiety, and the second from $\nu$(SnC) of the perpendicular bond (perhaps *trans* to the Sn–Cl bond), similar to that observed for $\nu(MX_3)$ in square planar $PtCl_3D^-$ and related compounds[19].

The configuration of the adducts may be deduced mainly from the infrared spectra of $Me_2SnCl_2$Acen. The assumed *trans*-dimethyl, *trans*-dichloro arrangement excludes the coordination of Acen as a bidentate chelating agent (through two oxygen or nitrogen atoms), as well as a monodentate ligand. A plausible way of accounting for the bonding situation is to assume the presence of six-coordinated tin(IV), arising from two additional Sn–N (or Sn–O) *trans* bonds, as illustrated by the polymeric structures shown in Fig. 2. The structural information inferred from the vibrational spectra of the other adducts is not inconsistent with the suggested configurations. In particular, the $Me_3SnCl$ and $MeSnCl_3$ groups are assumed to lie in a square plane, with T-shaped $C_3Sn$ and $SnCl_3$ groups.



(I) (II)

Fig. 2. Proposed configurations for diorganotin(IV) halide–Acen adducts.

Further support for the structures proposed above may be drawn from the Mössbauer data summarized in Table 2. The large quadrupole splittings which are observed for $Me_2SnCl_2$Acen, $Me_2SnBr_2$Acen, and $Bu_2SnCl_2$Acen (and their near identity) are consistent with the *trans* dialkyl structures proposed. It has previously been noted that hexacoordinate tin compounds with two alkyl or aryl ligands in the *trans* position and the remaining four ligands either O or N typically show quadrupole splittings of 3.8 to 4.1 mm/sec[30]. Conversely, if the two organic residues occupy *cis* positions relative to the O or N nearest neighbors, quadrupole splittings of 1.7 to 2.2 mm/sec are observed. From these systematics it is concluded that the three bisalkyl substituted six coordinate compounds all have the *trans* configuration. Such a configuration can also be assigned to $Ph_2SnCl_2$Acen, despite the somewhat smaller *QS* which is observed, in consonance with the *trans* structure assigned by Fitzsimmons *et al.*[30] to $Ph_2SnCl_2$Bipy and $Ph_2SnCl_2$Phen, which have quadrupole splittings of

3.90 and 3.70 mm/sec, respectively, at liquid nitrogen temperature.

At the present time it is not possible to effect a comparison of the Mössbauer parameters of $MeSnCl_3Acen$ and $Me_3SnClAcen$ with compounds of known structure since in our knowledge these are the first mono- and tri-alkyl sixcoordinate compounds which have been studied by γ-resonance spectroscopy. However, it is interesting to compare the two compounds to each other, since (presumably) the apical Acen moieties are the same in the two cases and the difference between the two compounds is in the makeup of the equatorial plane which involves one alkyl-three halogen and three alkyl-one halogen configurations, respectively. The smaller isomer shift observed for the monomethyl compound arises from the electron withdrawing properties of the Cl atoms compared to $CH_3$. This electron withdrawal decreases the $5s$ electron density on the tin atom since the electron density involved in the $sp^3d^2$ hybrid orbitals used to form the octahedral structure is transferred in part to the halogen atoms. By contrast, in $Me_3SnClAcen$, three of the four equatorial ligand atoms effectively share electrons with the central metal atom to a greater extent, thus increasing the $5s$ electron density on tin, and hence the isomer shift is approximately 0.5 mm/sec larger in the latter case, than in the former.

This rationalization is also reflected in the quadrupole splitting parameter. As a first approximation, the $QS$ in $R_3SnXL_2$ and $RSnX_3L_2$, of the presumed configurations (such as those of Fig. 2), should be nearly identical (ignoring, for example, steric consequences of the difference between R and X). However, due to the greater electron withdrawing effect of Cl compared to $CH_3$, the electric field gradient is smaller in $MeSnCl_3Acen$ than in $Me_3SnClAcen$. In fact, as has been noted by Greenwood and Ruddick[31], in octahedral molecules of the type $SnA_mB_{6-m}$ ($m = 1, \ldots, 6$) if all of the ligands have filled $p_\pi$ orbitals, no quadrupole splitting is generally resolvable in the Mössbauer spectrum, despite the absence of true cubic ($O_h$) ligand symmetry around the metal atom. Clearly in $MeSnCl_3Acen$ this situation is more nearly realized than in $Me_3SnClAcen$, and hence the smaller $QS$ in the former compared to the latter is consistent with the proposed stereochemistry.

The polymeric structure of these compounds is also clearly indicated by the temperature dependence data summarized in Fig. 3 and in Table 2. A number of earlier studies[32] have elucidated the relationship between the strength of intermolecular forces and the temperature dependence of the Debye–Waller factor extracted from Mössbauer measurements. Stated in its most succinct form, this relationship shows that the stronger the intermolecular forces (everything else being equal) the smaller is the slope $d \ln f/dt$, where $f$ is the recoil-free fraction of the Mössbauer transition. A comparison of this temperature dependence for $(CH_3)_3SnClAcen$, $(CH_3)_3SnNCO$[33], $(CH_3)_3SnClPy$[34], $(CH_3)_2Sn(OCHO)_2$[34], $(CH_3)_4Sn$[34] and $(CH_3)_3SnF$[35] is summarized in Fig. 3 in which the data have been normalized to 120°K to facilitate comparison between absorbers of different thickness. From this figure it is seen that the data for $(CH_3)_3SnClAcen$ are intermediate between those for $(CH_3)_3SnNCO$ (a weakly polymeric five coordinate polymer in the solid) and $(CH_3)_3SnF$ (a strongly polymeric five coordinate polymer in the solid). These results may be contrasted to the data for $(CH_3)_4Sn$ and $(CH_3)_3SnClPy$ on the one hand and $(CH_3)_2Sn(OCHO)_2$ on the other. Like tetramethyltin, $(CH_3)_3SnClPy$ is a monomeric solid with fivefold coordination around the metal atom[36], and N–Sn–Cl bond angle of 180° and an Sn–Cl bond distance of $2.43 \pm 0.06$ Å. In contrast, dimethyltin diformate has six-fold coordination

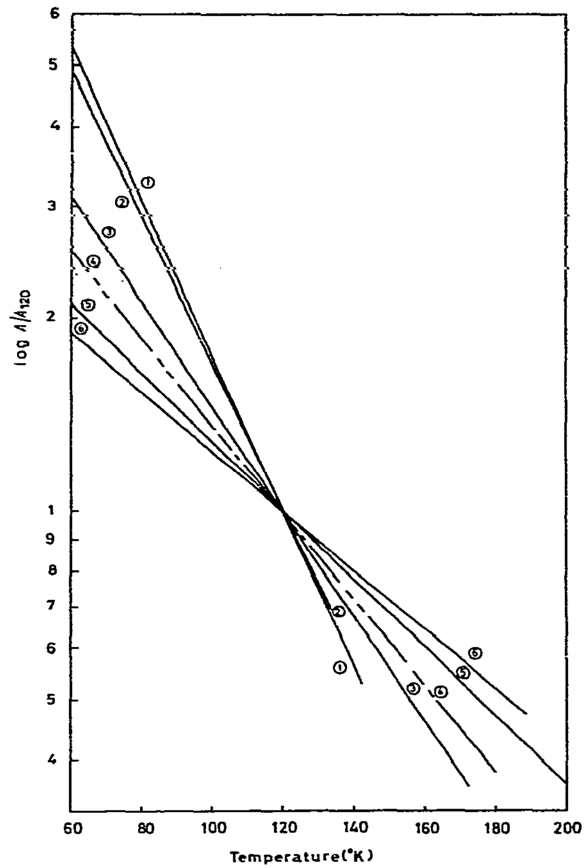


Fig. 3. The temperature dependence of log $A/A_{120}$ (the resonance absorption area at $T$ °K, $A$, normalized to the area at 120°K, $A_{120}$; $A$ is proportional to the recoilless fraction $f$, (see text) for the following compounds: 1, $(CH_3)_4Sn$ (ref. 34); 2, $(CH_3)_3SnClPy$ (ref. 34); 3, $(CH_3)_2SnNCO$ (ref. 33); 4, $(CH_3)_3SnClAcen$ (this work); 5, $(CH_3)_3SnF$ (ref. 35); 6, $(CH_3)_2Sn(OCHO)_2$ (ref. 34).

around the tin atom[37] with the two alkyl groups in *trans* position ($QS = 4.47 \pm 0.09$ mm/sec at 81°K), and is presumed to be polymeric.

From these results it may be inferred that the six-fold coordination around the metal atom in $(CH_3)_3SnClAcen$ is part of an extended polymeric network in which the metal atom phonon spectrum is governed largely by the extended intermolecular bonding forces between adjacent tin containing moieties. This structure is consistent with the interpretation of the infrared data cited above, and gives rise to a self consistent architecture of these organotin complexes with polydentate bases.

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