

MÖSSBAUER AND INFRARED SPECTROSCOPIC STUDIES ON COMPLEXES OF DIORGANOTIN(IV) WITH BIS(SALICYLIC ALDEHYDE) ETHYLENEDIIMINE

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SUMMARY

The infrared spectra and Mössbauer parameters of diorganotin(IV) complexes with the dianion of bis(salicylic aldehyde) ethylenediimine (Salen^{2-}) are discussed in the light of the molecular structure of $\text{Me}_2\text{SnSalen}$ derived from X-ray diffraction studies. Infrared data for $\text{Me}_2\text{SnSalen}$ are found to be fully consistent with the known distorted *trans*-octahedral configuration.

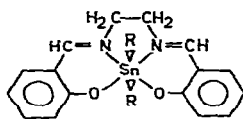
From the temperature dependence of the area under the Mössbauer resonance curve, the intensity asymmetry of the two components of the quadrupole split spectrum, and the value of the QS parameter, a reasonably complete description of the bonding, architecture and vibrational behaviour of $\text{Me}_2\text{SnSalen}$ emerges. The experimental data are consistent with the presence in the neat solid of monomeric molecular units, in which the bonding geometry around the central metal atom reflects the distorted *trans*-octahedral arrangement. The vibrational amplitude of the metal atom in the range $78 \leq T \leq 130$ K is essentially isotropic. The configuration of $\text{Ph}_2\text{SnSalen}$ is discussed on the basis of its IR spectrum and QS parameter.

INTRODUCTION

The interaction between tetradentate bases and organometal moieties or salts of non-transitional elements, has recently received much attention. First reports have dealt with the formation of adducts of organometal chlorides with bis(acetylacetonate) ethylenediimine (H_2Acen) and -1,2-diaminepropane^{1,2}, and of complexes $\text{R}_2\text{SnSalen}$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$)³ and $\text{Sn}^{\text{II}}\text{Salen}$ ³ [Salen^{2-} being the dianion of bis(salicylic aldehyde) ethylenediimine, H_2Salen]. The configuration of solid organotin halide- H_2Acen adducts has been investigated by infrared and Mössbauer spectroscopies^{4,5}, and their nature in solution phases was studied by electronic and PMR spectroscopies, as well as by osmometry and conductivity^{6,5}. Adducts $\text{SnCl}_4\text{-H}_2\text{Salen}$, $\text{R}_2\text{SnCl}_2\text{-H}_2\text{Salen}$, among others, were synthesized and studied^{7,8}. The preparation of $\text{R}_2\text{SnSalen}$ was subsequently repeated⁷⁻⁹, and other $\text{R}_2\text{Sn}(\text{ONNO})$ complexes were reported⁹. The configuration of $\text{R}_2\text{SnSalen}$ was investigated in solution

phase by PMR and electronic spectroscopies^{7,8}. Studies were also carried out on $\text{Sn}^{\text{IV}}\text{-Hal}_2\text{Salen}^{7,10,11}$, other $\text{Sn}^{\text{IV}}\text{Cl}_2(\text{ONNO})$ complexes¹¹ and $\text{Sn}^{\text{II}}\text{Salen}^{10}$. Lastly, the complexes $\text{R}_2\text{PbSalen}$ and R_2PbGbha ($\text{H}_2\text{Gbha} = 2,2'$ -bis-benzoxazoline) were prepared and investigated in the solid state and in solution phase by IR, electronic and PMR spectroscopies¹².

The configuration of solid $\text{R}_2\text{SnSalen}$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) has been studied in these laboratories by infrared and Mössbauer spectroscopies. On the basis of QS values, *trans*-octahedral structures of type (I) were tentatively assumed, as reported in a preliminary communication¹³.



(I) $\text{R}_2\text{SnSalen}$

This conclusion is in contrast to that drawn from PMR spectra, from which *cis*-configurations, and the existence of *cis/trans* isomers, was inferred^{7,8}. The recent determination of the crystal and molecular structure of $\text{Me}_2\text{SnSalen}$ by Randaccio *et al.*¹⁴ prompts us to report our detailed spectroscopic studies of two diorganotin-(IV)-Salen complexes.

EXPERIMENTAL

Pure reagents were used throughout the work; when necessary they were purified by standard procedures. Drying of the solvents was accomplished with molecular sieves. The organotin compounds were Fluka products. The ligand, H_2Salen , was prepared and purified as reported elsewhere¹².

Complexes $\text{R}_2\text{SnSalen}$ were synthesized by the usual NaOCH_3 method^{3,12}. Analytical data fully agree with the above 1/1 stoichiometries. M.p.: $\text{Me}_2\text{SnSalen}$, 257–258° dec. (lit.⁸ 254° dec.); $\text{Ph}_2\text{SnSalen}$, 255° dec. The complexes are stable when stored under anhydrous conditions, and slightly soluble in many dry organic solvents.

Extensive complex formation takes place in methanol (*i.e.*, the solvent in which the synthesis is effected), as demonstrated by the following electronic spectra (Beckman DK-2A, 10 mm cells, in rigorously anhydrous CH_3OH ; $c = 5.14 \times 10^{-5} \text{ M}$ for $\lambda > 250 \text{ nm}$, $c = 5.14 \times 10^{-6} \text{ M}$ for $\lambda < 250 \text{ nm}$): $\text{Me}_2\text{SnSalen}$: $\lambda_{\text{max}} = 345 \text{ nm}$ ($D = 0.60$); 270 (sh) (0.66); 256–260 (sh) (0.85); ~ 230 (0.22); $\text{Ph}_2\text{SnSalen}$: $\lambda_{\text{max}} = 345 \text{ nm}$ ($D = 0.57$); 270 (sh) (0.68); 260 (sh) (0.86); ~ 235 (sh) (0.23).

The shift to 345 nm of the 316 nm H_2Salen band indicates chelation of Salen^{2-} on $\text{R}_2\text{Sn}^{\text{IV}}$, according to the discussion concerning $\text{R}_2\text{PbSalen}^{12}$.

The vibrational spectra were taken with a Perkin-Elmer 457 instrument, in Nujol and hexachlorobutadiene (HCBd) mulls, in the range 4000–250 cm^{-1} , and with a Beckman IR 11 in the range 250–35 cm^{-1} on Nujol mulls 0.05 mm thick, using 0.05 mm Nujol as reference. Vibrational bands are as follows; (s=strong; v=very; m=medium; w=weak; sh=shoulder; br=broad. Starred figures refer to HCBd mulls).

1. H_2Salen (250–35 cm^{-1} range): 217 m, 102 vw cm^{-1} (see Ref. 12 for bands in the 4000–250 cm^{-1} range).

2. $\text{Me}_2\text{SnSalen}$: 3100–2800*, group of weak bands; 1620 vs, 1595 m, 1535 s, 1525 (sh), 1460* s, 1450* s, 1405 s, 1355 w, 1340 s, 1315 m, 1260 vvw, 1240 m, 1215 w, 1190 s, 1150 s, 1130 m, 1090 w, 1045 m, 1030 m, 995 w, 985 vw, 950 w, 900 m, 850 w, 780 m, 760 s, 750 (sh), 740 m, 640 w, 630 vw, 600 m, 570 m, 555 (sh), 520 w, 485 vw, 460 m, 445 vw, 400 m, 370 w, 345 w, 285 m, 186 m, 160 w, 58 vw cm^{-1} .
3. $\text{Ph}_2\text{SnSalen}$: 3100–2800*, group of weak bands; 1620 s(br), 1600 s, 1535 s, 1515 (sh), 1480* m, 1460* s, 1440* vs, 1425* m, 1405* s, 1345 (sh), 1340 m, 1300 m, 1260 vw, 1240 vw, 1185 m, 1150 s, 1130 m, 1090 w, 1070 vw, 1060 vvw, 1040 vw, 1030 w, 1020 vw, 990 w, 970 vvw, 950 w, 900 m, 850 w, 780 w, 750 s, 730 s, 695 s, 655 w, 635 w, 615 vvw, 600 s, 575 vw, 530 w, 460 s, 400 m, 365 m, 340 m, 300 m, 236 m(br), 187 (sh), 169 m cm^{-1} .

The Mössbauer measurements were carried out on thin sample absorbers using the techniques described earlier^{15,16}. A variable temperature Dewar vessel fitted with carbon and platinum resistance thermometers and a calibrated iron/constantan thermocouple, was used for the temperature dependence studies. This arrangement permitted temperature control to within $\pm 0.5^\circ$ for the 10 to 20 h periods required for data accumulation. Spectrometer calibration was effected using 0.8 mm NBS SR M iron foil and ultra pure BaSnO_3 as described earlier^{17-19,*}.

Data reduction was effected using a least squares fitting program which fits two Lorentzian maxima while permitting line position, line width and effect magnitude to vary as independent parameters. This program was run on the Rutgers-Princeton IBM 360/91 computer and requires about 5.4 sec for execution. Approximately 10^6 counts per channel were scaled at each velocity point in the 199 point spectrum. All isomer shifts are quoted with respect to the center of a $\text{BaSnO}_3/\text{BaSnO}_3$ room temperature spectrum, and are thus directly comparable (within the experimental uncertainty of ± 0.020 mm/sec) with data reported with respect to SnO_2 .

DISCUSSION

According to L. Randaccio and his coworkers¹⁴, the unit cell of $(\text{CH}_3)_2\text{SnSalen}$ contains two molecules, whose structures are essentially identical. In summary, the environment of tin in the neat solid $(\text{CH}_3)_2\text{SnSalen}$ consists of distorted octahedra, with ONNO and Sn atoms located in the equatorial plane, and the two methyl groups in a *trans* configuration with significant departure from linearity in the C-Sn-C bond axis [see structure (II) following]. The various Sn-O and Sn-N bond lengths range between 2.19 and 2.27 Å, and Sn-C between 2.07 and 2.19 Å. Bond angles in the equatorial plane are largely distorted (O-Sn-O 127° and 122° in the two molecules, respectively; O-Sn-N 78° , 81° and 81° , 83° ; N-Sn-N 73° and 74°). The Sn-C bonds are symmetrically bent towards the oxygens (O-Sn-C angles ranging between 91° and 78°), C-Sn-C being 160° and 162° respectively.

cis-Structures, such as those advanced by Murray *et al.*⁷ and Tanaka *et al.*⁸ on the basis of multiple signals in the PMR spectra, may perhaps exist in solution because of solvation effects. On the other hand, one must be very careful in dealing with solutions of $R_2\text{SnSalen}$, owing to the facile hydrolysis of these compounds. In

* The authors are indebted to Dr. R. Gallagher of Bell Telephone Labs for making this material available to us.

fact, from solutions of $R_2SnSalen$ in pure, commercial C_6H_6 , $CHCl_3$, CCl_4 , we recovered white solid residues which were identified as $(Me_2SnO)_n$ and $(Ph_2SnO)_n$ from their IR spectra²⁰. The occurrence of double signals and of two sets of values for $J(^{119}Sn-C-H)^{7,8}$ could then be understood if the species $Me_2SnSalen$, H_2Salen and solvated Me_2Sn^{IV} were formed in the wet solvent. Further, a pure *cis*-dimethyltin(IV) configuration in octahedral $Me_2SnSalen$ is inconsistent with the lower set of reported $J(^{119}Sn-C-H)$, which range between 81 and 84 Hz^{7,8}. These would correspond to about 37.5–39% *s*-character in the Sn–C bonds, *i.e.*, to a C–Sn–C angle slightly smaller than 180° .

The IR spectra of $R_2SnSalen$ in the $4000-700\text{ cm}^{-1}$ range are fully consistent with chelation by $Salen^{2-}$ on R_2Sn^{IV} , as implied by the molecular structure of the Me_2Sn^{IV} derivative outlined above. The pattern is similar to that of $R_2PbSalen$ (if

TABLE 1

MÖSSBAUER PARAMETERS FOR H_2Salen COMPLEXES OF DIORGANOTIN(IV), $R_2SnSalen$

Compound	T (K)	IS ^a (mm/sec)	QS (mm/sec)	Γ_{Ave} ^b (mm/sec)	$\frac{\log \epsilon(T)^f}{\log \epsilon(120\text{K})}$	$R = \frac{I_+^d}{I_-}$
$Me_2SnSalen$	78	1.13	3.46	0.874	2.712	1.010
	85	1.16	3.46	0.867	2.482	1.056
	90	1.11	3.46	0.855	2.308	0.921
	100	1.16	3.44	0.870	1.930	1.008
	122	1.15	3.44	0.882	0.896	0.985
	130	1.16	3.44	0.864	0.419	1.620
$Ph_2SnSalen$	84	0.88	2.84	0.975		

^a Shift with respect to the center of a $BaSnO_3$ spectrum at $295 \pm 1\text{ K}$. ^b Average width at half height of the absorption peaks. ^c The log of the area under the resonant curve at $T\text{ K}$ normalized to the log of the area at 120 K. ^d Asymmetry parameter (see text), corrected for solid angle and crystal orientation effects.

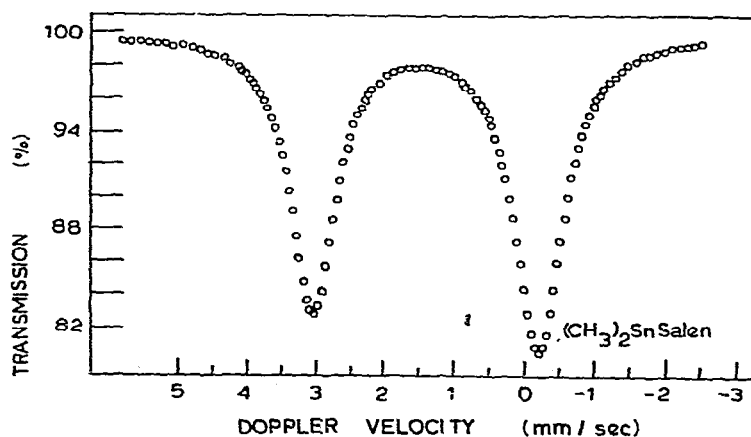


Fig. 1. Mössbauer spectrum of $(CH_3)_2SnSalen$ at 78 K. The Doppler velocity is shown relative to the centroid of a $BaSnO_3/BaSnO_3$ spectrum at room temperature. The intensity asymmetry in the two components of the quadrupole split doublet is temperature independent and arises from preferential crystal orientations effects in the sample.

allowance is made for phenyl vibrations of the diphenyl derivatives), which was extensively discussed in an earlier communication¹².

Skeletal vibrational modes involving Sn–O, Sn–N and Sn–C bonds are expected to occur in the low-energy region. The bands at 600 and 400 cm^{-1} may be tentatively attributed to Sn–O and Sn–N modes^{21,22}. Vibrations of $\text{Ph}_2\text{Sn}^{\text{IV}}$ ²³ in $\text{Ph}_2\text{SnSalen}$ could contribute to the band at 460 cm^{-1} , and occur at 236 and 169 cm^{-1} (other phenyl ring vibrations of $\text{Ph}_2\text{Sn}^{\text{IV}}$ ²⁴, identified in the spectrum of $\text{Ph}_2\text{SnSalen}$, are at 1480, 1425, 1060–1070, 1020, 730 and 695 cm^{-1}). The band of $\text{Me}_2\text{SnSalen}$ at 570 cm^{-1} is safely attributed to $\nu_{\text{as}}(\text{SnC}_2)$ ^{21,22}, while that occurring at 520 cm^{-1} cannot be due to $\nu_{\text{s}}(\text{SnC}_2)$, since a corresponding band appears at 530 cm^{-1} in $\text{Ph}_2\text{SnSalen}$. This is fully consistent with the “quasi” linear configuration of the CH_3SnCH_3 moiety¹⁴.

The numerical data extracted from the Mössbauer effect measurements are summarized in Table 1, and a typical spectrum is shown in Fig. 1. The isomer shift (+1.130 mm/sec) and quadrupole splitting (3.464 mm/sec) data of $\text{Me}_2\text{SnSalen}$ at 78 K are in good agreement with the values reported from this laboratory in an earlier communication¹³. The isomer shift is typical of that observed for other dialkyltin(IV) species and confirms the assignment made previously. In accord with earlier observations, neither parameter (*IS* or *QS*) is sensitive to temperature variation in the region $78 \leq T \leq 130$ K, and the least squares best fit values for the isomer shift and quadrupole splitting over the indicated temperature range are 1.146 ± 0.018 and 3.450 ± 0.010 mm/sec, respectively.

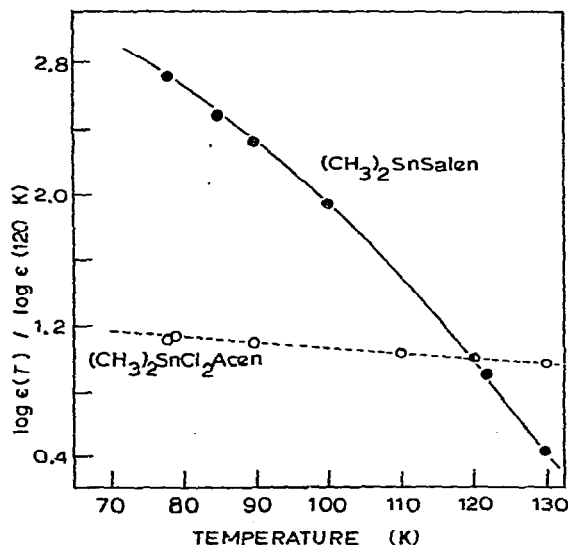


Fig. 2. Temperature dependence of the resonance effect magnitude in $(\text{CH}_3)_2\text{SnSalen}$, compared with analogous data for $(\text{CH}_3)_2\text{SnCl}_2\text{H}_2\text{Acen}$ (polymeric). The data have been normalized to 120 K to facilitate intersample comparison.

The temperature dependence of the area under the resonance curve is shown graphically in Fig. 2, in which the data have been normalized to the value at 120 K to facilitate comparison with literature data. In contrast to similar temperature

dependence data reported earlier²⁵, the present results (on a semilogarithmic plot) are not well fitted by a straight line relationship, but rather show a downward curvature over the indicated temperature range. The linear relationship expected for the $\ln(\text{Area})$ vs. temperature plot is derived from the assumptions of a Debye model behavior²⁶ for which:

$$\text{Area} \propto \exp - \left\{ \frac{3}{2} \frac{E_R}{k \cdot \theta_M} + \frac{6E_R}{k \cdot \theta_M^2} \cdot T \right\} \quad (1)$$

whence:

$$d \ln(\text{Area})/dT = -6E_R/k \cdot \theta_M^2 \quad (2)$$

where E_R is the recoil energy of the ^{119}Sn atom given by $E_R = E_\gamma^2/2M \cdot c^2$, and θ_M is a "Mössbauer temperature" which is related to the rigidity of the lattice in which the Mössbauer atom is embedded. The origin of the departure from linearity of the present data may be due to the breakdown of the Debye model assumptions or of the thin-absorber approximation used to fit the experimental data. The latter assumption is, however, likely to be valid in view of the line width data summarized in Table 1.

In any event, the present data on the temperature dependence of the recoil-free fraction are clearly indicative of the absence of any strong intermolecular bonding forces between adjacent $\text{Me}_2\text{SnSalen}$ units. In other words, in agreement with Rاندaccio¹⁴, the molecular unit is clearly monomeric, with the two oxygen and two nitrogen atoms in the equatorial plane about the metal atom belonging to one Salen^{2-} moiety. There is no evidence in these data for bridging between adjacent metal atoms via a heteroatomic bridging species such as that which has been postulated in other alkyltin(IV) species such as $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$ ²⁷, $(\text{CH}_3)_3\text{Sn}(\text{CN})$ ²⁸, $(\text{CH}_3)_3\text{SnClH}_2\text{Acen}^4$ and $(\text{CH}_3)_2\text{SnCl}_2\text{H}_2\text{Acen}^4$. The absence of significant intermolecular bonding forces is also borne out by the fact that the far infrared spectrum in the 35 to 150 cm^{-1} region shows no significant absorption in $\text{Me}_2\text{SnSalen}$. Such modes are expected to be associated with intermolecular interactions in polymeric organotin(IV) species, and their absence in the infrared would be consistent with the conclusions drawn from Mössbauer data.

An additional parameter which can be extracted from the temperature dependent Mössbauer spectra is related to the anisotropy of the vibrational amplitude of the metal atom parallel with and perpendicular to the symmetry axis through the metal atom. This vibrational anisotropy is reflected as a temperature-dependent asymmetry in the relative intensity of the two components of the quadrupole split Mössbauer spectrum, and is commonly referred to as the Gol'danskii-Karyagin effect²⁹. Previous work reported from this laboratory has shown that this effect is particularly pronounced in *trans* octahedral dialkyltin(IV) compounds such as $(\text{CH}_3)_2\text{SnF}_2$ ³⁰ and $(\text{C}_4\text{H}_9)_2\text{SnF}_2$ ³¹, in which there is a pronounced difference in the nature of the chemical bond which binds the metal atom to the nearest neighbor atoms lying in the equatorial plane compared with the bonding in the axial direction.

The relative intensities of the two components of the quadrupole split doublet spectrum, given by the parameter $R = I_+/I_-$ (where I_+ and I_- are the intensities of the resonance peak at more positive and more negative velocity than the spectrum centroid, respectively) are shown in Fig. 3. The data have been corrected for a residual crystal orientation caused asymmetry (recognized by its temperature independence)

and for nonlinearity in the spectrometer base line (due to solid angle effects and corrected for by an appropriate blank experiment without absorber). It is seen from Fig. 3 that in the temperature range $78 \leq T \leq 130$ K there is no Gol'danskii-Karyagin asymmetry observable in the spectra, and that the mean value over this range corresponds to unity with a standard deviation of less than 5%.

These results can be understood in terms of crystallographic structural analysis¹⁴ referred to above, which reveals a severe distortion of the symmetry of the nearest neighbor environment around the metal atom from an idealized O_h configuration. This distortion influences the angular dependence of the vibrational amplitude in two ways. First, the absence of a linear C-Sn-C arrangement gives rise to a signifi-

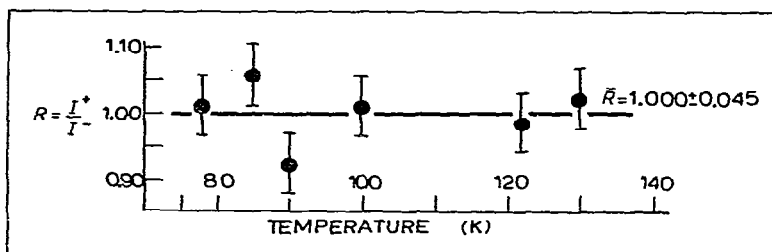
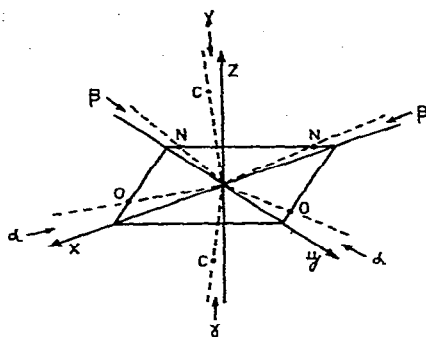


Fig. 3. Intensity ratio parameter R of $(\text{CH}_3)_2\text{SnSalen}$ plotted as a function of temperature in the range $78 \leq T \leq 130$ K. These data suggest an isotropic vibrational amplitude of the ^{119}Sn atom in the sample compound over the quoted temperature range, as discussed in the text.

cant departure from cylindrical geometry through the metal atom, and hence reduces the amplitude vector projected on the pseudo-rotational symmetry axis. Since the vibrational amplitude parallel to the (idealized) C-Sn-C axis is presumed to be larger than that perpendicular to this axis, the effect of closing the C-Sn-C bond angle to $\sim 161^\circ$ is to reduce the amplitude projection on the idealized symmetry axis. Second, the distortion of the bond angles which describe the interaction between the metal atom and the nearest neighbor ligand atoms lying in the pseudo equatorial plane gives rise to a weakening of the bonding interaction perpendicular to the (idealized) C-Sn-C bond axis. This weakening is expected to result in an increase in the vibrational amplitude in the equatorial plane. The combination of these two effects is seen to give rise to a vibrational amplitude which can be considered isotropic within the accuracy of the present data.

Returning now to the known geometry of $\text{Me}_2\text{SnSalen}$ derived from the X-ray diffraction data, it is possible to rationalize the observed quadrupole splitting of 3.46 mm/sec at 78 K (this value is assumed to be essentially identical at room temperature, the conditions under which the diffraction data were obtained) in terms of the point charge formalism³²⁻³⁴ by taking into account the directions of the orbitals involving the bonding electrons of the metal atom^{35,36}. The principal axes are chosen as indicated in (II), in order to give vanishing off-diagonal components of the electric field gradient tensor, and to have $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ ³⁶ ($V_{ii} = \partial^2 V / \partial i^2$, V being the potential). From the molecular structure of $R_2\text{SnSalen}$ it is seen that two pairs of coordinate axis angles, (α, α) and (β, β) in (II), can be made mutually equal by a proper choice of the x and y axes, so that $V_{xx} = V_{yy}$, and the asymmetry parameter³⁶, η , vanishes:



(II)

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} = 0 \quad (3)$$

From eqn. (3), and the expression for QS , it follows^{32-34,36} that:

$$QS = K \cdot V_{zz} \propto 2(3 \cos^2 \gamma - 1) \cdot [R] + 4(3 \cos^2 90^\circ - 1) \cdot [X] \quad (4)$$

where $[R] = -0.31$ mm/sec for $R = \text{alkyl}$ and -0.20 mm/sec for $R = \text{phenyl}$ ³⁴. The value of $[X]$ may be taken as 0.63 mm/sec (calculated for $X = \text{Cl}$)³⁴, assuming that the contribution of the $ONNO$ donor atoms to the field asymmetry corresponds nearly to that due to four chlorides. Assuming $\gamma = 10^\circ$, from eqn. (4) it follows for $R = \text{Me}$:

$$QS = 3.76 \cdot [R] - 4[X] = |3.68| \quad (5)$$

and, for $R = \text{Ph}$, $QS = |3.27|$. These calculated QS values are slightly different from those obtained for a regular octahedral configuration, for which $QS = 4([R] - [X])$ ^{32,33}. The experimental $QS = 3.46$ mm/sec for $\text{Me}_2\text{SnSalen}$ fits satisfactorily to the calculated value, despite the assumptions made in the above treatment. It is also consistent with the QS values measured for a number of six-coordinated *trans*-di-alkyltin(IV) derivatives³⁷.

Finally, it is appropriate to consider the implications of the quadrupole splitting value observed for $\text{Ph}_2\text{SnSalen}$ (Table 1). The value of 2.84 mm/sec considerably differs from the point charge value above, and is intermediate between that observed for *cis* octahedral and for *trans* octahedral diphenyltin(IV) compounds having 6-fold coordination³⁷. It can be inferred from these systematics that the introduction of two phenyl groups into the quasi axial (*trans*) positions with respect to the metal atom would involve considerable steric interaction between the organic ligand and the tetradentate Salen^{2-} moiety. The expected consequence of this interaction would be to distort the molecule from its near octahedral configuration by increasing one, or more likely two, of the Sn-O or Sn-N bonds. The extent to which this structure can still be adequately described as a quasi octahedral configuration cannot be settled on the basis of the presently available data, and a full X-ray diffraction study of $\text{Ph}_2\text{SnSalen}$ is awaited to elucidate this interesting problem.

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