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Complexes of Organometallic Compounds. XLVIII.
Mössbauer and Other Studies on Pyrazine Derivatives of Tin(IV) Compounds. A Relationship between Isomer Shift and Charge on Tin

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Adducts $RSnCl_3 \cdot pyz$ (R = Me, Bu^n, Oct^n, Ph; pyz = pyrazine) have been synthesized and characterized in the solid state. It has been determined that $RSnCl_3 \cdot pyz$ are polymeric compounds, where the ligand acts as bridging bis-monodentate and the tin atoms attain the coordination number six. This has been deduced from: i) temperature dependent Mössbauer spectroscopy; ii) the correlation between Mössbauer isomer shift, δ, and electrical charge on tin, Q_{Sn}, concerning pyrazine adducts of $RSnCl_3$ and others; iii) an infrared study of the coordinated ligand in $RSnCl_3 \cdot pyz$.

*Other implications of the Mössbauer T dependent study (*e.g., *the decrease of the Debye temperature in $RSnCl_3 \cdot pyz$ with increasing mass of R), as well as of the δ/Q_{Sn} correlation (*e.g., *the occurrence of linear dependences as function of the Sn coordination number, using Q_{Sn} from the method of Jolly and Perry [11, 12]), are presented and discussed.*

The skeletal configuration around tin is lastly studied by point-charge model calculations of Mössbauer partial quadrupole splitting due to pyz/2, and of ΔE of $RSnCl_3 \cdot pyz$. A structure with meridional Cl_3 and cis-*N_2 is proposed.*

Introduction

The present work has been originally undertaken as a part of a research program on RSn^{IV} derivatives [1], with the aim of investigating the solid state nature and configuration of novel pyrazine adducts of mono-organotin(IV) trichlorides ($RSnCl_3 \cdot pyz$, 1:1; R = Me, Bu^n, Oct^n, Ph; pyz = pyrazine, 1,4-diazine). Incidentally, it was expected that the experimentation and interpretation of data concerning the interaction with tin of the simple bis-monodentate ligand pyrazine, having two heterocyclic nitrogen donor atoms, could be a reference study for researches on complexes of organotin(IV) with purine and pyrimidine bases, which are under way in our laboratories [2].

During the course of the Mössbauer work we observed a peculiar characteristic of the temperature dependence of the recoil free fraction of $RSnCl_3 \cdot pyz$ (R = alk), which has suggested to expand the experimental to known adducts $SnCl_4 \cdot pyz$ and $SnCl_4 \cdot (pyz)_2$ [3], with the aim of gaining further knowledge on the correct interpretation of such type of temperature dependence data. Besides, we have determined the possibility of rationalizing Mössbauer isomer shift parameters of $RSnCl_3 \cdot pyz$ as well as of $Snhal_4 \cdot pyz$ [3], $SnCl_4 \cdot (pyz)_2$ [3] and $Ph_2SnCl_2 \cdot pyz$ [4, 5] in order to get information on the coordination number of tin(IV) (and consequently on the polymeric or monomeric nature of the compounds under study) by means of a relationship between isomer shift and the calculated electrical charge on tin. An infrared study of the denticity of the ligand in $RSnCl_3 \cdot pyz$ has been also carried out. Lastly, a possible skeletal configuration in the neighborhood of tin has been proposed through the point-charge model rationalization of the Mössbauer quadrupole splitting.

Experimental

Organotin reagents were gifts from Schering AG and Ciba-Geigy, or purchased from Fluka as was the ligand pyrazine. The solvent cyclohexane (C. Erba) has been dried with molecular sieves and de-oxygenated with N_2. The adducts $RSnCl_3 \cdot pyz$ have been prepared by mixing equimolar cyclohexane solutions of organotin and ligand under stirring, and by filtering off the obtained white solids. Analytical data are in Table I. Other compounds here investigated have been obtained by literature methods [3, 4], and their nature checked by elemental analysis and m.p.

The Mössbauer spectra have been measured at constant acceleration, triangular waveform, by the apparatus and procedures described earlier [1, 6]. Base line correction was effected (with a computer program) by folding the two specular spectra obtained in each run. Fig. 1 shows the quality of the

TABLE I. Analytical Data [Found/(Calcd.)%].

Compound[a]	M.p. (°C)	C	H	Cl	N	Sn
$MeSnCl_3 \cdot pyz$	155–58	18.82 (18.76)	2.23 (2.20)	33.40 (33.22)	8.63 (8.75)	36.65 (37.07)
$Bu^nSnCl_3 \cdot pyz$	117–21	26.70 (26.53)	3.69 (3.62)	29.00 (29.36)	7.87 (7.73)	32.65 (32.76)
$Oct^nSnCl_3 \cdot pyz$	94–98	34.65 (34.45)	4.75 (5.06)	25.63 (25.42)	6.53 (6.70)	28.72 (28.37)
$PhSnCl_3 \cdot pyz$	245–50	31.23 (31.42)	2.32 (2.37)	27.89 (27.83)	7.19 (7.33)	30.96 (31.05)

[a] Pyz = pyrazine.

TABLE II. Mössbauer Data for $RSnCl_3 \cdot pyz$ and Other Pyrazine Complexes.
(sample thickness = 0.5 mg $^{119}Sn/cm^2$)

Temp.[a] (°K)	A[b]	Temp.[a] (°K)	A[b]
$MeSnCl_3 \cdot pyz$ (δ[c] = 0.99; ΔE[d] = 2.35)		$PhSnCl_3 \cdot pyz$ (δ = 0.91; ΔE = 2.10)	
78	40.36	79	32.02
85	33.64	85	29.40
103	31.29	106	24.73
126	27.68	129	20.00
149	23.92	150	16.74
$Bu^nSnCl_3 \cdot pyz$ (δ = 1.13; ΔE = 2.32)		$SnCl_4 \cdot pyz$ (δ = 0.52[e]; ΔE = 0.92[e])	
80	38.95	80	43.81
86	36.02	84	42.66
106	30.62	103	37.26
127	25.23	126	32.31
137	23.66	148	27.56
150	20.66		
$Oct^nSnCl_3 \cdot pyz$ (δ = 1.03; ΔE = 2.19)		$SnCl_4 \cdot (pyz)_2$ (δ = 0.50[f]; ΔE = 0.64[f])	
80	37.86	79	34.92
86	35.28	106	28.68
104	28.89	127	25.54
129	23.04	137	23.43
137	20.73	148	20.37
150	18.65		
		$Ph_2SnCl_2 \cdot pyz$ (δ = 1.36[g]; ΔE = 3.10[g])	

[a] Within about 0.5°. [b] Total area under the resonant peaks, mm s^{-1} ($A = \pi/2 \times \epsilon \times \Gamma\ 1/2$, where ϵ is per cent effect and $\Gamma\ 1/2$ is full width at half height of the Lorentzian fits to experimental data: $\Gamma\ 1/2$ values generally lie around 0.9 mm s^{-1}, while being 1.0÷1.2 for $MeSnCl_3 \cdot pyz$). [c] Isomer shift with respect to RT $BaSnO_3$. [d] Nuclear quadrupole splitting, mm s^{-1}; these parameters are essentially invariant with temperature (±0.02 mm s^{-1} for $SnCl_4 \cdot (pyz)_2$ only). [e] Lit. [3]: δ = 0.38; ΔE = *ca.* 0.60. [f] Lit. [3]: δ = 0.43; ΔE = 0. [g] Measured at liquid N_2 temperature. Lit. [5]: δ = 1.32; ΔE = 3.00.

obtained data, while Table II and Fig. 2 report the experimental Mössbauer parameters and temperature dependent data.

The infrared spectra have been measured with Perkin-Elmer Mod. 457 and Beckman IR 11 instruments in the 4000–250 and 500–80 cm^{-1} regions respectively (the latter by courtesy of dr. G. Faraglia, Istituto di Chimica, Università di Padova), in Nujol or hexachlorobutadiene mulls between CsI or polythene disks. Relevant bands are listed in the following (s = strong, m = medium w = weak, bd = broad, sh = shoulder; some assignments are in parentheses, while absorptions due to coordinated pyrazine are underlined):

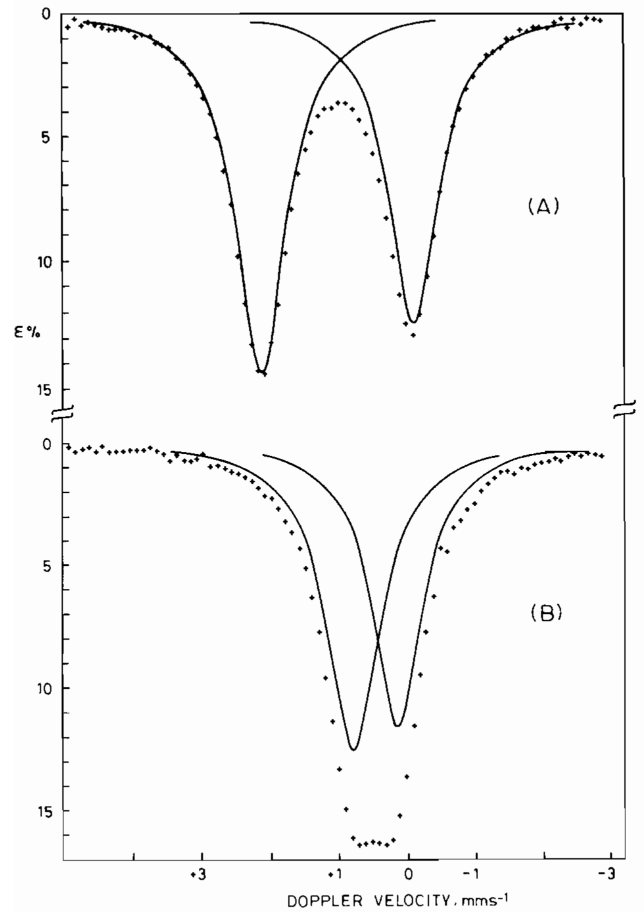

Figure 1. Mössbauer spectra, at liquid N_2 temperature, of: (A) $Oct^nSnCl_3 \cdot pyz$; (B) $SnCl_4 \cdot (pyz)_2$. Experimental crosses come from folding of the two specular halves. Full lines are computed Lorentzians. The occurrence of a small, but measurable, quadrupole splitting is evidenced in (B).

$MeSnCl_3 \cdot pyz$: 3130 w; 3100 vw; 3060 w; 1425 vs; 1170 ms; 1120 vs; 1065 vs; 810 mw; 770 w, bd; 540 mw [ν(SnC)]; 476 vs; 334 m; 290 s, bd [$\nu(SnCl_3)$]; 223 w; 209 w; 203 w; 174 mw; 151 s [$\delta(SnCl_3)$?].
$Bu^nSnCl_3 \cdot pyz$: 3120 w; 3110 w; 3090 w; 2960 m; 2930 mw; 2870 w; 1465 mw; 1455 mw; 1420 vs; 1375 mw; 1350 sh; 1235 w; 1225 w; 1170 s; 1120 vs; 1095 w; 1060 vs; 1035 w; 1020 m; 880 m; 820 s; 720 w, bd; 675 m; 600 vw [ν(SnC)]; 478 vs; 395 w; 336 s; 275 vs, bd [$\nu(SnCl_3)$]; 198 w; 178 mw; 165 m bd [$\delta(SnCl_3)$?]; 149 w; 146 w.
$Oct^nSnCl_3 \cdot pyz$: 3130 m; 3110 m; 3070 mw; 2950 s, bd; 2860 s; 1470 m; 1420 vs; 1380 w; 1365 sh; 1175 s; 1115 vs; 1065 vs; 1045 mw; 1035 mw; 1025 w; 990 w, bd; 895 m; 830 w; 810 s; 725 w; 665 s; 595 w, bd [ν(SnC)]; 476 vs; 467 m; 435 w; 380 w; 350 mw; 340 w; 325 mw; 290 vs, bd [$\nu(SnCl_3)$]; 266 m; 241 m; 212 mw; 155 s, bd [$\delta(SnCl_3)$?]; 95 w, bd.

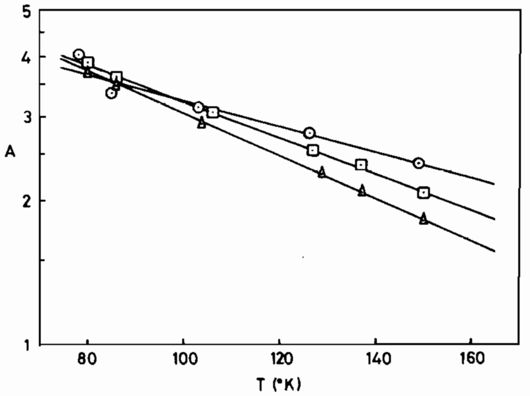

Figure 2. Temperature dependence of lnA for: ⊙: $MeSnCl_3 \cdot pyz$ (correlation coefficient r = 0.968; slope b = -6.507×10^{-3}); ⊡: $Bu^nSnCl_3 \cdot pyz$ (r = 0.998; b = -8.792×10^{-3}); ⍋: $Oct^nSnCl_3 \cdot pyz$ (r = 0.999; b = -10.123×10^{-3}). Data for other compounds here studied are: $PhSnCl_3 \cdot pyz$, r = 0.999, b = -8.985×10^{-3}; $SnCl_4 \cdot pyz$, r = 1.000, b = -6.764×10^{-3}; $SnCl_4 \cdot (pyz)_2$, r = 0.991, b = -7.399×10^{-3}.

$PhSnCl_3 \cdot pyz$: 3130 vw; 3110 vw; 3070 vw; 3060 vw; 1470 m (Ph ring vibr.); 1435 ms (Ph); 1420 vs; 1195 w (Ph); 1175 s; 1120 vs; 1065 vs; 1020 w (Ph); 1000 mw (Ph); 895 w (Ph); 810 s; 790 w; 735 w, bd; 720 ms (Ph); 700 w; 690 s (Ph); 475 vs; 447 vs (Ph); 340 s; 294 s, bd [$\nu(SnCl_3)$]; 232 m (Ph t-mode); 212 m (Ph, u); 188 s (Ph, x); 177 s; 156 w; 128 ms [$\delta_s(SnCl_3)$]; 110 vw.

Discussion

From data in Table I it is inferred that $RSnCl_3 \cdot pyz$ have 1:1 organotin chloride: ligand composition. The characterization of these adducts is performed by discussing the collected experimental data, as well as related correlations with calculated quantities.

Temperature Dependence of the Recoil Free Fraction

This is treated here according to Herber, Hazony *et al.*, whose approach is amply illustrated in the previous paper [1] (see also Refs. [7]).

The relationship between the ln of the total area, A, under the resonant signal (which is proportional to the γ quanta recoil free fraction f_a in the thin absorber approximation) and the temperature is a straight line for all compounds in Table II and Fig. 2 (see also legend to the Figure). This means that measurements have been performed in the high temperature range ($T \geqslant \theta/2$, θ being the Debye temperature), for which:

$$f_a = \exp - \left\{ \frac{3}{2}\frac{E_R}{K\theta} + \frac{6E_R}{K\theta^2} T \right\} \qquad (1)$$

$$d(\ln f_a)/dT = -\frac{6E_R}{K\theta^2} \qquad (2)$$

where $E_R = E_\gamma^2/2Mc^2$, M being the effective vibrating mass associated to the resonant atoms.

Slopes in Fig. 2 (and legend) would be within ranges typical for compounds with high intermolecular forces [1], *i.e.*, for solid state polymers [8]. This would mean that pyrazine acts as bis-monodentate in $RSnCl_3 \cdot pyz$, in the same way as in $Snhal_4 \cdot pyz$ [3] and $Ph_2SnCl_2 \cdot pyz$ [4, 5], so that Sn would be six-coordinate in all these adducts.

It seems interesting to comment further the trend shown by the three adducts $AlkSnCl_3 \cdot pyz$, Fig. 2, where the slope increases from Me to Oct^n derivatives; according to Eq. (2), it is inferred a progressive diminution of θ by increasing size of the alkyl radical, and the latter effect (and not the parallel increase of the formula weight) governs the slope magnitude. As a consequence, the extent of intermolecular interaction would be decreasing from Me to Oct^n derivatives. This circumstance would be in some way responsible of the magnitude of the parameters δ and ΔE of $Oct^nSnCl_3 \cdot pyz$ (Table II; these have been repeatedly determined on several different samples, since they appeared anomalous with respect to those of Me and Bu^n compounds) as well as of the m.p. values of $AlkSnCl_3 \cdot pyz$ (Table I). It may be worth to recall that the trend discussed above (increase of slope d (ln A)/dT with increasing formula weight; see legend to Fig. 2) holds for all terms of the homologous series $ASnCl_3 \cdot pyz$ (A = Alk, Ph, Cl).

The case of $SnCl_4 \cdot (pyz)_2$ may be discussed mainly in connection with data for $SnCl_4 \cdot pyz$. On the basis of vibrational spectroscopy, it has been deduced that these compounds are, respectively, a six-coordinate monomer, with monodentate pyrazine and a six-coordinate polymer with bis-monodentate ligand [3]. The fact that $SnCl_4 \cdot (pyz)_2$ shows a slope d (ln A)/dT which is only slightly larger than that of the polymer $SnCl_4 \cdot pyz$ (Fig. 2, legend) may be in principle interpreted in terms of a polymeric structure for $SnCl_4 \cdot (pyz)_2$ too, which could be attained, inter alia, by assuming one bridging and one terminal pyrazine, with seven coordinate tin in a monodimensional polymer chain. This is at variance with the vibrational studies referred to above, so that the actual structure of $SnCl_4 \cdot (pyz)_2$ remains an open question*.

Correlation of ^{119m}Sn Isomer Shift with Atomic Charge on Sn

The reason why this correlation was attempted lies in the previously observed approximate dependence of tin isomer shift, δ, on average electronegativity of ligands in derivatives of RSn^{IV} [9], and in the circumstance that δ for $RSnCl_3 \cdot pyz$ are functions of the radical bound to the metal (Table II). To the purpose, the dependence of δ from the atomic charge on tin has been here determined, in consonance with principles employed by Huheey and Watts [10] for $Snhal_4$, $Snhal_6^{2-}$ and Sn^0. In the present context the atomic charges have been calculated by the empirical equation proposed by Jolly and Perry [11, 12], based on the equalization of valence state electronegativities of atom partners in each bond. This procedure has been previously used for correlating atomic charges with ESCA binding energies [11, 12], also for tin compounds [13]. The equation for a given couple of atoms, n and m, linked by a chemical bond, is the following:

$$\frac{7.3(h_m + h_n)}{(N_{nm})^{0.7}} q_{mn} + h_m \sum_{i \neq n} q_{mi} - h_n \sum_{i \neq m} q_{ni} =$$

$$= \chi(p)_n - \chi(p)_m + \frac{S_{nm}}{(1 + \pi_{nm})^{0.7}} (\chi(s)_n - \chi(p)_n) -$$

$$- \frac{S_{mn}}{(1 + \pi_{nm})^{0.7}} (\chi(s)_m - \chi(p)_m) + C_n h_n F_n -$$

$$- C_m h_m F_m \qquad (3)$$

where h is a parameter proportional to the difference between valence state ionization potentials, Iv, and electron affinities, Ev (taken principally from Hinze and Jaffè [14]); N_{nm} is the bond order, and π_{nm} the π-bond order; q_{nm} and related symbols are charge transferred from one atom to another; $\chi(p)$ and $\chi(s)$ are p and s orbital electronegativities [13]; S_{nm} and similar symbols are fractional s characters used in given bonds (*e.g.*, of the σ orbital used by atom n in being linked to atom m); 7.3, 0.7 and C are constants adjusted in order to give the best fit between charges and ESCA binding energies; F are formal charges [11, 12]. An equation as (3) is set up for any bond, and the obtained series is then solved for the unknowns q_{ji}; then, the charge on a given atom is obtained by [11, 12]:

$$Q_n = F_n + \Sigma q_{ni} \qquad (4)$$

It must be recalled here that the equation proposed by Jolly and Perry [11] for the electronega-

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*A referee has pointed out that, in the context of our qualitative approach, in the series $ASnCl_3 \cdot pyz$ it is worth considering the quasi-linear dependence of d ln f_a/dT from 1/M (M being the formula weight), inverted with respect to expectation from Eq. (2), while the data point for $SnCl_4 \cdot (pyz)_2$ lies well outside the line. This would be consistent with a steady diminution of θ (*i.e.* of the intermolecular intra-unit vibrational frequency ω_L [7]) taking place in $ASnCl_3 \cdot pyz$ parallel to the steady increase of M, in such a way that $M\omega_L^2$ decreases in the same direction [7]. Parameters of $SnCl_4 \cdot (pyz)_2$ would not have such a connection with those of members of the homologous series, due to the substantially different solid state nature.

tivity of an orbital of a given atom, from which Eq. (3) is obtained upon an equalization procedure, essentially corresponds to the definition by Huheey [15], *i.e.*, $\chi_{orb} = \chi_{fixed} + \delta(I_v - E_v)$, where

$$\chi_{fixed} = \frac{I_v + E_v}{2},$$

and δ is the partial charge on the given atom. The reason why in this work the procedure of Huheey has not been followed lies in the circumstance that it requires the use of electronegativities of lone pairs and vacant orbitals, as defined by Jaffè *et al.* [16], when treating donor–acceptor bonds, and these data are rather intriguing to deal with; instead, the procedure becomes quite straightforward by the empirical approach of Jolly and Perry, according to which one electron is apportioned per atom in the case of a dative bond, consequently attributing the resulting formal charges to the two bonded atoms. Further work is under way on the application of the Huheey formalism to the calculation of fractional charges also for donor–acceptor complexes, which will be published in due time.

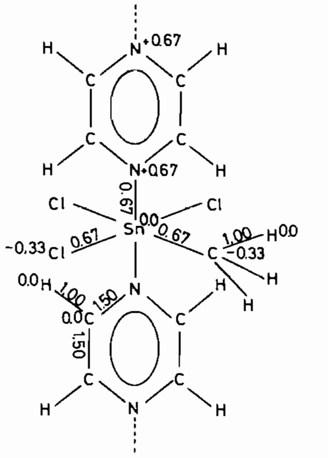

Figure 3. Example of formal charges and bond orders for $MeSnCl_3 \cdot pyz$ (considered a polymer with six-coordinate Sn) according to the procedure by Jolly and Perry [11, 12]. Formal charges on atoms bound to tin are obtained by apportioning one electron each to N and Sn for N→Sn bonds, then redistributing the 2– charge on tin to the six atoms bound to it. Formal charge of tin is zero, being assumed that only s and p orbitals are employed in its bonds [12]. Other compounds in the series are treated similarly. In the case of $SnCl_4 \cdot (pyz)_2$, considered as a six-coordinate monomer, formal charges of pyrazine nitrogens not bound to tin are taken as 0.00. This Figure has no relation with the structure of the compound.

For five-coordinate Sn, considering that the compounds are monomeric units, two cases have been taken into account: a) trigonal bipyramidal configuration [12], with the more electronegative atoms $N^{+}_{tr\,tr\,tr\,\pi}$ and $Cl_{s^2p^2p^2p}$ [14] in axial position: formal charges, Sn = 0.00, N = +0.70, Cl_{axial} = –0.30, $Cl_{equatorial}$ = –0.13 (as C_{eq}); bond orders, axial = 0.70, equatorial = 0.87. b) with equal distribution of s and p character between the five bonds to Sn: formal charges, Sn = 0.00, N = +0.80, Cl(C) = –0.20; bond order = 0.80.

For seven-coordinate Sn, in (polymeric?) $SnCl_4 \cdot (pyz)_2$, with equal distribution of s–p character between the seven bonds to Sn: formal charges, Sn = 0.00, N = +0.57, Cl = –0.43; bond order = 0.57.

The calculations of Q_j by Eqns. (3) and (4) have been performed for pyrazine complexes by the program CHELEQ [11, 12], written by Perry on the basis of the equalization procedure described above, and modified by us in order to suit our purposes. The case of six-coordinate tin (bis-monodentate ligand in a polymeric configuration) has been considered first, and the input data (formal charges and bond orders) have been attributed as described in Fig. 3. Results are in Fig. 4; it appears that charges on tin [17] do not vary sensibly with the nature of the alkyl radical bound to the metal, which forbids, by this method, the wanted correlation δ/Q_{Sn} for $RSnCl_3 \cdot pyz$. It has been instead observed that all pyrazine complexes here considered show a linear dependence δ/Q_{Sn} for six-coordinate Sn (Fig. 4). Data for $SnBr_4 \cdot pyz$ and $SnI_4 \cdot pyz$ fall on the straight line when the constant C [11, 12] for Br and I is taken as 2.7 instead of 1.6 [18]. Points for complexes of $RSnCl_3$ and Ph_2SnCl_2 lie outside the line when tin is taken as five-coordinate, and the same occurs for $SnCl_4 \cdot (pyz)_2$ on the hypothesis of seven coordination for tin. Taking into account the octahedral structures previously proposed for $Snhal_4 \cdot pyz$ and $Snhal_4 \cdot (pyz)_2$ [3], and also for $Ph_2SnCl_2 \cdot pyz$ [4, 5], the correlation shown in Fig. 4 strongly suggests the occurrence of six-coordination for tin in $RSnCl_3 \cdot pyz$, and consequently the polymeric nature of these adducts in the solid state, in consonance with the results on the temperature dependence of the γ-ray recoil-free fraction.

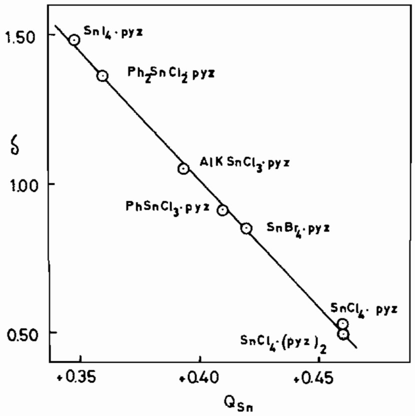

Figure 4. Relation δ *vs.* Q_{Sn} for pyrazine complexes [17]. Values of δ are in Table II, and in Ref. 3 for $SnBr_4$ and SnI_4 derivatives. Six coordinate Sn: ⊙ (correlation coefficient = 0.965; average values for Alk $SnCl_3 \cdot pyz$ are Q_{Sn} = +0.393, δ = 1.05).

Infrared Spectra

The vibrational study of Goldstein and Unsworth [3] on halotin–pyrazine complexes, on the basis of group theory arguments, stated that: i) in the mid-IR, coincidences are found between Raman and IR bands for $Snhal_4 \cdot (pyz)_2$, while absent in spectra of $Snhal_4 \cdot$ pyz, from which it is inferred that the ligand is monodentate in the first adducts (which are then monomolecular species) and bridging bis-monodentate in the second (which have the nature of solid state polymers); ii) in the low energy region, the occurrence of only one mode attributable to ν(Snhal) and ν(SnN) vibrations in each adduct is consistent with octahedral structures, with pyrazine nitrogens in *trans*-position and equatorial halide atoms.

In the IR spectra of $RSnCl_3 \cdot pyz$, reported in this paper under Experimental, bands related to $RSnCl_3$ moieties have been satisfactorily identified, in a special way for R = Me, Bu^n, Ph, according to assignments discussed in earlier studies [19] (see assignments, Experimental). Internal pyrazine fundamentals, attributed to monodentate pyrazine [3] in $SnCl_4 \cdot (pyz)_2$, are generally absent in $RSnCl_3 \cdot pyz$ (*e.g.*, vibrations at 1490, 1350, 1230, 1085, m, and the group at 740 m, 700 w, 640 m: in the place of the latter three, there are other frequencies in varying number); instead, all vibrations attributed to bis-monodentate pyrazine [3], for example in $SnCl_4 \cdot$ pyz, are found in $RSnCl_3 \cdot pyz$ in the range ~3140–~460 cm^{-1}. It is then inferred that the ligand is bis-monodentate also in $RSnCl_3 \cdot pyz$, so that these adducts would be polymers with six-coordinate tin, in consonance with findings from T-dep. and δ / Q_{Sn} data discussed above.

In the far-IR region (see listing under Experimental, this paper), it is seen that the broadness of the $\nu(SnCl_3)$ band for $RSnCl_3 \cdot pyz$ does not allow any hypothesis about the configuration of the $SnCl_3$ skeleton. Besides, no bands attributable to $\nu(SnN_2)$ modes are identified with reasonable certainty in the 200–250 cm^{-1} region, where found for $Snhal_4 \cdot (pyz)_2$ and $SnCl_4 \cdot$ pyz [3], nor at lower energy. A common band occurring in $RSnCl_3 \cdot pyz$ at 330–350 cm^{-1} seems to be too energetic in order to be assigned to $\nu(SnN_2)$ modes. These facts forbid any choice, on the basis of infrared spectroscopy, between the three possible skeletal configurations I, II and III, Fig. 5, of $CSnCl_3N_2$ atoms in $RSnCl_3 \cdot pyz$.

Point-charge Model Calculations of the Skeletal Configuration

This may be instead attempted by the rationalization of nuclear quadrupole splittings, ΔE (Table II), using the point-charge model formalism [20] and related calculations according to Equations reported elsewhere [6, 20].

The partial quadrupole splitting [20] (p.q.s.) due to bound pyrazine, $1/2\ e^2\ |Q|([pyz/2] - [hal])$, may be calculated using $Ph_2SnCl_2 \cdot pyz$ as estimator compound. It has been observed earlier that the latter compound is a solid state polymer [4, 5] and consequently has to show an octahedral type structure around Sn, which has been confirmed here in the preceding; besides, its experimental δ and ΔE values (Table II) are consistent with a *trans*-Ph_2 configuration [21, 22], and the occurrence of two skeletal modes $\nu(SnCl_2)$, sym and asym, in its infrared spectrum [4] strongly suggests a *cis*-structure for the Cl atoms. Point-charge calculations based on this octahedral structure, considered to be regular with *trans*-C_2, *cis*-N_2 and *cis*-Cl_2 atoms, as well as on the value ΔE = (+)3.10, gave $1/2\ e^2\ |Q|([pyz/2] - [hal]) = -0.35$ mm s^{-1}.

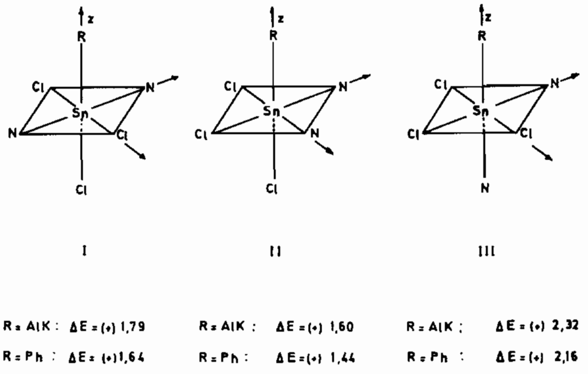

Figure 5. Point-charge calculations for ideal octahedral configuration of polymers $RSnCl_3 \cdot pyz$. P.q.s. used (1/2 e^2 [Q] units): ([Alk] – [hal]), −1.03 [20]; ([Ph] – [hal]), −0.95 [20]; ([pyz/2] – [hal]), −0.23 obtained by using $SnCl_4 \cdot$ pyz as estimator compound (see text).

Adducts $Snhal_4 \cdot$ pyz also may be used as estimator compounds for obtaining pyrazine p.q.s., in view of their very probable *trans*-N_2 octahedral configuration [3]. In the context of their ΔE magnitude, it is worth observing that values measured in this work for $SnCl_4 \cdot$ pyz and $SnCl_4 \cdot (pyz)_2$ (Table II) are much more self-consistent than previous data [3], in view of the similarity of Sn neighborhood in both compounds [3]. The occurrence of measurable ΔE for $SnCl_4 \cdot (pyz)_2$ is clearly evidenced by Fig. 1. As to the sign to be attributed to their experimental ΔE, chemical intuition suggests that it is positive (*i.e.*, the principal component of the electric field gradient tensor, V_{zz}, is negative), since electrical charge would be concentrated along the Z-axis where N atoms effect charge donation to tin. In such a context it is calculated, for example, $1/2\ e^2\ |Q|([pyz/2] - [hal]) = -0.23$ mm s^{-1} using as estimators (+)ΔE of $SnCl_4 \cdot$ pyz (Table II) and $SnBr_4 \cdot$ pyz [3]. These two compounds would be preferred, as estimators of p.q.s., since their polymeric nature would be very similar to that of $RSnCl_3 \cdot pyz$.

Using the above p.q.s. values for the calculations of ΔE of $RSnCl_3 \cdot pyz$, values consistent with structure III, Fig. 5, are obtained. Data pertaining to p.q.s. = –0.23 are reported in Fig. 5 as an example. A pertinent comment to this deduction would consider that structure III corresponds to that assumed for $RSnX_3 \cdot L_2$ adducts, L_2 being a bidentate base [23]; this configuration has been advanced also where L is a monodentate ligand [24] and, in any case, structures showing *cis*-L–L have been preferred [24] whenever the technique used in the investigation gave unequivocal answers [6, 9, 20, 24].

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17 Q_{Sn} are as follows: a) six-coordinate Sn: $RSnCl_3 \cdot pyz$: R = Me, Q_{Sn} = +0.392; Bu^n, +0.393; Oct^n, +0.393; Ph, +0.410; $Ph_2SnCl_2 \cdot pyz$, +0.360; $SnCl_4 \cdot (pyz)_2$, +0.459; $Snhal_4 \cdot pyz$: hal = Cl, +0.459; Br, +0.420; I, +0.348 (C = 2.7 for Br and I); by restricting the calculation to Sn and atoms directly bound to it, slightly different values of Q_{Sn} are obtained (*e.g.*, for $SnCl_4 \cdot pyz$, atoms $SnCl_4N_2$, Q_{Sn} = +0.481). b) Five coordinate Sn; trigonal bipyramidal configuration with apical N and Cl atoms: $MeSnCl_3 \cdot pyz$, Q_{Sn} = +0.333; $PhSnCl_3 \cdot pyz$, +0.355; $Ph_2SnCl_2 \cdot pyz$, +0.288. With equal distribution of s–p character between the five bonds: $MeSnCl_3 \cdot pyz$, Q_{Sn} = +0.346; $PhSnCl_3 \cdot pyz$, +0.367; $Ph_2SnCl_2 \cdot pyz$, +0.306. c) Seven-coordinate Sn: $SnCl_4 \cdot (pyz)_2$, Q_{Sn} = +0.479.

18 It may be mentioned that, using the value 1.00 for the three constants in Eq. (3), unrealistic values of Q_j are obtained, or, alternatively, the program does not converge.

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