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NOTE

INVESTIGATIONS ON ETHYLTIN CHLORIDE PYRIDINE COMPLEXES

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In a previous report on the PMR spectra of the 1/1 and 1/2 methyltin halide-pyridine complexes[1] the sterical configuration of the former was accepted to be trigonal bipyramidal and for the latter an octahedral configuration was supposed. These configurations were those that had been derived from an X-ray investigation for the $(CH_3)_3SnCl \cdot Py$ adduct by Hulme and from IR spectroscopic data[2,3] by Beattie and coworkers. The coupling constant data in our work, therefore were interpreted in terms of a rehybridization of the bonding orbitals of tin to respectively sp^3d and sp^3d^2 type orbitals, and it was pointed out that, on the assumption that the percent *s*-character should be divided equally over the five, respectively six orbitals, this was in apparent disagreement with the generally accepted[4,5] view that the J(Sn–C–H) values increase with increasing percent *s*-character of the tin orbital. Bolles and Drago[6] then argued that the actual structure in the five-coordinated compounds should be intermediate between a tetrahedral configuration with the C–Sn–Cl angle about 109° and a pure trigonal bipyramidal configuration with 90° C–Sn–Cl angles, depending on the donor strength of the Lewis base, the stronger yielding the highest distortion of the tetrahedral configuration. In the pentacovalent sp^3d orbitals of tin, the percent *s*-character can be considered[7,10] to concentrate in the orbitals in the trigonal plane, giving them about sp^2 character, whereas the axial bonds should be of the *dp* type: $(d_{z^2}+p_z)$. For the octahedral compounds, with sp^3d^2 hybrids, the axial Sn–C bonds use orbitals with essentially *sp* character, the other are then d^2p^2 type orbitals. These models could explain the increase of the tin–proton coupling constants.

TABLE 1

COUPLING CONSTANTS Sn–H (IN CPS) OF SOME ETHYLTIN CHLORIDES AND THEIR PYRIDINE COMPLEXES[a]

Compound	$J(^{117,119}Sn–C–H)$	$J(^{117,119}Sn–C–C–H)$
Et_3SnCl	48 /50	88.8/ 92.8
$Et_3SnCl \cdot Py$	53.6/56.8	94.4/ 98.4
Et_2SnCl_2	49.5/51.7	124.8/130.8
$Et_2SnCl_2 \cdot 2Py$	70.5/74	152 /160

[a] Spectra of the pure liquids recorded with a Varian V.4300 B spectrometer at 56.4 MHz. The high melting point of $EtSnCl_3 \cdot 2Py$ does not allow measurements in the liquid state.

The IR data are, however, less easy to interpret because the assignments are not always straightforward and many spectra were incomplete. The IR data have however clearly proved that in $R_3SnCl \cdot X$ the three R groups tend to be coplanar and that for $R_2SnCl_2 \cdot X_2$ the two R groups occupy the axial positions, the four other groups forming a trans configuration[2,3].

This investigation of the PMR, IR and Raman spectra of the ethyltin chloride–pyridine complexes is part of a program to study the use of spectroscopic methods in this field of organotin chemistry. The spectroscopic data are given in tables 1 and 2.

TABLE 2

IR AND RAMAN FREQUENCIES FOR THE Sn–Cl AND Sn–C STRETCHING VIBRATIONS[a]

Compound	Sn–Cl stretching (cm^{-1})		Sn–C stretching (cm^{-1})			
	IR	Raman (ρ)	Symm.		Antisymm.	
			IR	Raman (ρ)	IR	Raman (ρ)
Et_3SnCl		321 (0.18)	488	491 (0.05)	518	524 (0.74)
$Et_3SnCl \cdot Py$		263 (0.3)	481	481 (0.08)	521	521 (0.7)
Et_2SnCl_2	300 (s) 330 (a, s)	310	495	490	530	528
$Et_2SnCl_2 \cdot 2Py$	220	217	480	481	530	
$EtSnCl_3$	360	370 (0.2)	515	520 (0.35)		
$EtSnCl_3 \cdot 2Py$	310 265 (?)	309 280 (?)	497	498		

[a] IR spectra recorded with a P.E. model 225 spectrometer. Raman spectra recorded with a Coderg spectrometer and an O.I.P. He/Ne laser.

The J(Sn–C–H) values show the expected increasing trend in going from $(C_2H_5)_3SnCl$ or $(C_2H_5)_2SnCl_2$ to the complexes and the values for the diethyltin complex are seen to be higher than those for the triethyltin compound. This is in agreement with the linearity relation between J(Sn–C–H) and the per cent *s*-character and thus also with the theories explained above[6,7]. The J(Sn–C–C–H) values, however, are seen to be relatively less sensitive to complex formation. This confirms the conclusions of some recent studies[8,9] that in the Sn–H coupling over two bonds the Fermi contact term is dominant, whereas for the coupling over three bonds both the Fermi contact term and the electron orbital term are important. The simultaneous use of IR and Raman spectroscopy, including depolarization ratio measurements allowed the assignments to be made with more confidence than in previous reports[3]. The number of the fundamental frequencies observed for Sn–C and Sn–Cl bonds and their relative intensities in the various compounds allows confirmation of the sterical conclusions mentioned above[2,3]. The suggestion that ν(Sn–Cl) should decrease with complexation[3] is confirmed by our data. It might seem evident to explain this by the decreased bond strength of the pd, resp. p^2d^2 orbitals as compared with the original (distorted) sp^3 orbitals. This argument is, however, not backed by the data of the ν(Sn–C) vibration, which show also a decrease on complex formation. This apparent anomaly is the subject of further investigations in progress in our laboratory. The assignment of some of the low frequencies observed to Sn–N vibrations is another topic for further study.

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