Synthesis and Mössbauer Spectra of Five- and Six-coordinate Complexes of Di- and Tri-organotin Chlorides with *p*-Anisaldehydethiosemicarbazone

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Abstract

Complex formation between di- and tri-organotin chlorides and the potentially bidentate ligand, *p*-anisaldehydethiosemicarbazone (abbreviated as PAT), has been examined. In all the cases, addition complexes of a 1:1 stoichiometry are formed. The PAT ligand functions as a bidentate donor towards the di-organotin chlorides resulting in octahedral geometries, whereas in the adducts of the tri-organotin chlorides with PAT, the tin atom adopts a trigonal bipyramidal coordination and the PAT monodentate. Elemental analysis confirmed the stoichiometries of the complexes and their solid state configurations have been studied by ^{119m}Sn Mössbauer and far infrared spectroscopy.

Introduction

PAT exhibits interesting coordinating behaviour in metal complexes as can be observed from the few structural studies reported in the literature [1].

The investigation we have carried out on organotin(IV) chloride with PAT has revealed that the chelating properties of the N and S ligands are influenced by the nature of the R group as well as by the nature of the organotin component. An unusual unidentate behaviour has been observed by us for PAT in $R_3SnClPAT$ (where R = Me, Bu and Ph).

Recently, we have reported the synthesis, the characterization by IR spectra, elemental analysis, magnetic measurements, and electronic spectra of Mn(II), Fe(II), Co(II) and Ni(II) with PAT [1] and the fungitoxicity of the complexes on pathogenic fungi.

The complex behaviour of this ligand with organotin compounds has not been studied as far as we know. Hence, the present work deals with the synthesis and characterization by IR and ^{119}Sn Mössbauer techniques of two sets of new adducts of formulas R_2SnCl_2PAT and $R_3SnClPAT$ (R = Me, Bu, Ph).

Results and Discussion

Mössbauer Spectra

The six-coordinate complexes

The Mössbauer spectra parameters for the series R_2SnCl_2PAT compounds (R = Me, Ph and Bu) are collected in Table I. It is evident from these data that all the complexes in this series have quadrupole splittings around 4.0 mm s^{-1}, characteristic of *trans* SnR_2 octahedral geometries [2, 3]. However, the ΔE_q values observed for Bu_2SnCl_2PAT and Ph_2SnCl_2PAT suggest a CSnC bond angle of less than 180° and by implication, greater 5s character in the Sn–C bonds [4]. Consequently, the compounds adopt distorted octahedral configurations [2].

Complexes of Ph_2SnCl_2 with bipyridine and phenanthroline have *trans* SnR_2 configuration [5], but with other nitrogen donors Ph_2SnCl_2 yields *cis* complexes [6]. It has been suggested that the formation of *trans* and *cis* isomers depends on the size of the donor ligand, but it is probably more accurate to consider the mutual influence of all the ligands on the tin atom [7, 8]. This includes both steric and electronic effects. The butyl group is no less bulky than a phenyl group, but being a better sigma donor, tends to acquire most of the tin 5s character so that a linear C–Sn–C structure results. The normal electronic factors are thus manifested in the isomer shift and quadrupole values. Thus the variation in ΔE_q values also indicates that the C–Sn–C bond angles decrease in the order $SnMe_2 < SnBu_2 < SnPh_2$ confirming an octahedral distortion for Bu_2SnCl_2PAT and Ph_2SnCl_2PAT complexes.

The five-coordinate complexes

The Mössbauer shift (δ) and quadrupole splitting ΔE_q parameters observed for $R_3SnClPAT$ (R = Me, Ph and Bu) in Table I compare favourably with those reported [9] for similar 1:1 adducts of triorganotin chlorides which have trigonal bipyramidal structures. Three possible isomers are available for this type of structure as shown here (**I**, **II**, **III**).

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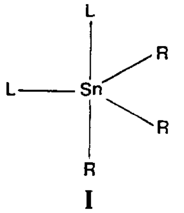
TABLE I. Analytical and Mössbauer Data for Complexes

Complex	Appearance	Microanalysis data[a]					Tin 119 Mössbauer data[b]	
		C	H	N	S	Cl	IS	QS
Me_2SnCl_2PAT	yellow	30.62 (30.77)	3.84 (3.96)	9.56 (9.79)	7.42 (7.46)	15.93 (16.55)	1.55	4.10
Bu_2SnCl_2PAT	yellow	39.65 (39.77)	5.63 (5.65)	7.43 (8.18)	5.84 (6.23)	12.96 (13.84)	1.64	3.91
Ph_2SnCl_2PAT	yellow	45.61 (45.56)	3.72 (3.79)	7.46 (7.59)	5.58 (5.78)	12.52 (12.83)	1.60	3.86
$Me_3SnClPAT$	yellow	35.23 (35.25)	4.77 (4.89)	10.20 (10.28)	7.94 (7.83)	8.64 (8.69)	1.28	3.12
$Bu_3SnClPAT$	yellow	47.21 (47.14)	7.32 (7.11)	7.72 (7.85)	5.83 (5.98)	6.60 (6.64)	1.29	3.18
$Ph_3SnClPAT$	yellow	54.44 (54.49)	4.38 (4.37)	7.05 (7.06)	5.28 (5.38)	5.83 (5.97)	1.31	3.28

[a] Calculated values in parentheses. [b] Values at 80 K in mm s^{-1}.



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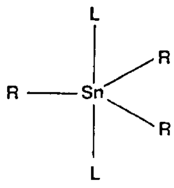

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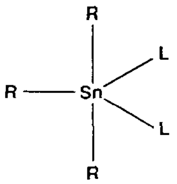


III

In the Mössbauer spectrum, each of these possible isomeric forms would be expected to show different quadrupole splitting values [10, 11]. For isomers of type **I**, the range of ΔE_q is 1.7–2.3 mm s^{-1}, for type **II** 3.0–3.9 mm s^{-1}, and for type **III** 3.5–4.1 mm s^{-1}. The ΔE_q values for our complexes all fall in the range 3.12–3.28 mm s^{-1} indicating structure **II** with essentially planar R_3Sn moieties.

The symmetry of the charge distribution about tin in these structures is C_{3v}. We therefore envisage the Sn–C bonds to possess maximal s character compared to other tin–ligand bonds. However, on the basis of greater electron withdrawing capability of the phenyl group over butyl and methyl, the isomer shift (δ) suffers a decrease from Ph > Bu > Me in accord with the greater sensitivity of δ to changes in s-orbital occupancy than p-orbital occupancy. The greater electronegativity of the phenyl group also results in the p electron imbalance [12] becoming more negative and consequently, also the field gradient. This leads to a more positive value of ΔE_q as observed (*i.e.* ΔE_q $Ph_3SnClPAT > Bu_3SnClPAT > Me_3SnClPAT$).

Infrared Spectra

In this section, we describe the IR spectra of the free ligand and the complexes (Table II). The complete analogy of the IR spectra of the ligand is noteworthy and is as previously described [1].

The spectra similarity of the complexes R_2SnCl_2-PAT (R = Me, Bu and Ph) can be justified by a

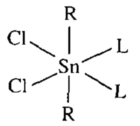
TABLE II. Selective IR Spectra

Complex	ν(NH_2) asy.	ν(NH) sym.	ν(NH)	ν(C=C) + ν(C=N)	ν(C=S)	ν(Sn–N)	ν(Sn–S)	ν(Sn–Cl) asy.	ν(Sn–Cl) sym.	ν(Sn–Cl)
Me_2SnCl_2PAT	3425vs	3250s		1640s		560vs	391s	360s	345s	
Bu_2SnCl_2PAT	3425vs	3250s		1643s		600vs	394s	355s	340s	
Ph_2SnCl_2PAT	3425vs	3250s		1645s		560s	415s	367s	342s	
$Me_3SnClPAT$	3425vs	3250s		1642s	782s	564s				321s
$Bu_3SnClPAT$	3425vs	3250s		1642s	782s	605s				335s
$Ph_3SnClPAT$	3425vs	3250s		1641s	782s	580s				325s
PAT (Ligand)	3425vs	3250s	3140s	1620s	782s					

similar stereochemistry involving the (C=N) and (C=S) group behaviour of the ligand. One important band at 3140 cm^{-1} in the uncomplexed ligand has disappeared due to the enolization of the (C=S) on complex formation. The ν(C=S) of the NH_2 moiety also disappeared for the same reason. Changes also occur in the spectra frequencies of (C=N) and (C=C) due to the involvement of (C=N) in complex formation. Those changes which affect the position and intensities of the ν(C=N) and (C=S) frequencies suggest the participation of the N and S atoms of these groups in the coordination to tin in accord with values previously reported for metal complexes with the same ligand [1]. Consequently, bands in the ranges 560–605 and 390–415 cm^{-1} have been assigned to ν(Sn–N) and ν(Sn–S) respectively [1, 13].

The spectra of the series $R_3SnClPAT$ (R = Me, Bu and Ph) as compared to the series R_2SnCl_2PAT show a complete absence of ν(Sn–S) absorption, implying the non-participation of the S atom in the coordination to tin.

Finally, the ν(Sn–Cl) came at the expected regions. For the series R_2SnCl_2PAT, the bands in the ranges 355–360 and 340–345 cm^{-1} have been ascribed to unsymmetric and symmetric ν(Sn–Cl) vibrations respectively [13] indicating *cis* positions for the halogens [14].



The other bands in the range 320–335 cm^{-1} have been assigned to ν(Sn–Cl) in the series $R_3SnClPAT$ [13].

Experimental

The ligand, *p*-anisaldehydethiosemicarbazone (Compound W (ref. 1)) was prepared by the standard method [15].

Synthesis of Complexes

The complexes were prepared generally by mixing equimolar quantities of the organotin chloride with the ligand in ethanol solution and refluxing. A typical procedure is thus described.

Preparation of $(CH_3)_2SnCl_2PAT$

The diorganotin(IV) adduct was prepared by adding an ethanol solution of Me_2SnCl_2 (2.20 g, 0.01 mol) to an ethanol solution of the ligand (2.09 g, 0.01 mol). The solution was refluxed with constant stirring for 3 h. The complex was recovered from the solution by filtration followed by washing with ether and drying *in vacuo* over $CaCl_2$.

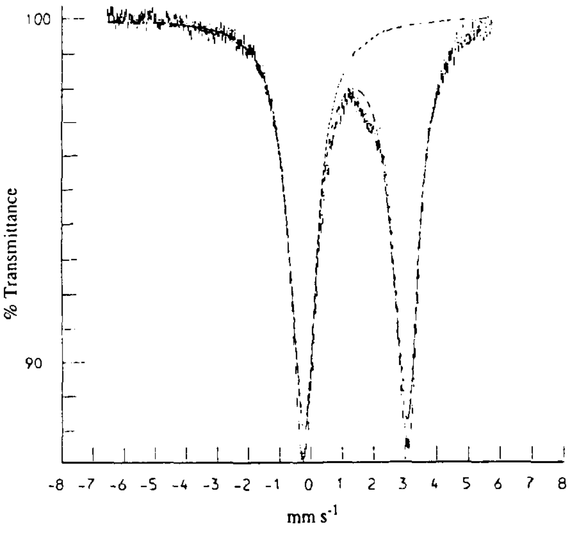


Fig. 1. The Mössbauer Spectrum of $Ph_3SnClPAT$.

Instruments

Elemental analyses were made on Perkin-Elmer Model 240G automatic equipment.

Infrared spectra were recorded on a Perkin-Elmer Model 983G spectrophotometer in CsI pellets in the range 4000–180 cm^{-1}.

The procedures employed for the collection of ^{119}Sn Mössbauer spectra are as in the literature [16]. Spectra for the complexes were recorded at room temperature accumulating a minimum of 10^6 counts per channel, and subsequently fitted to Lorentzian lineshapes by the usual least-squares method. The results are summarized in Table I and a typical Mössbauer spectrum is shown in Fig. 1. The solid line represents the computer fit to the data.

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