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Synthesis, Vibrational and Mössbauer Spectra Studies of Complexes of Organotin Chlorides and 2-pyridinecarboxaldehyde Thiosemicarbazone

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Abstract

The complex formation between organotin chlorides and 2-pyridinecarboxaldehyde thiosemicarbazone (PT) has been investigated. In only one case is a substitution reaction observed whereas in all other cases, 1:1 addition complexes are formed. The solid state configurations of the complexes have been studied by ^{119m}Sn Mössbauer and far infrared spectroscopy. The chelating ligand (PT) functions as a bidentate ligand towards diorganotin chlorides giving octahedral coordination geometry around the tin atom.

Introduction

Iron(II) complexes of 2-pyridinecarboxaldehyde thiosemicarbazone in the ratio 1:2 [1, 2] have been found to possess a substantial inhibitory effect against tumor cells. Previously we have reported the synthesis and characterization of Co(III) complexes of 2-pyridinecarboxaldehyde thiosemicarbazone ligand in the ratio 1:2 with different anions [3]. Although the coordination behaviour of nitrogen, oxygen and sulphur donor ligands towards organotin chlorides and derivatives has been studied extensively [4–8] no studies of organotin complexes with the same ligand have been reported as far as we know.

In these complexes, the PT ligand functions as a tridentate ligand towards Co(III) with two nitrogens and one sulphur as donor atoms, but in the present case, it functions as a bidentate ligand with the ring nitrogen and the terminal NH_2 as donor atoms. We thus present in this paper, synthesis and characterization of diorganotin chlorides with 2-pyridinecarboxaldehyde thiosemicarbazone.

Experimental

The ligand, 2-pyridinecarboxaldehyde thiosemicarbazone was prepared by standard methods [9].

Synthesis of Complexes

The syntheses were all similar and details are presented in Table I. The general procedure is as follows; with diorganotin dichloride 1:1 adducts of the diorganotin dichloride R_2SnCl_2 (R = Oct, Bu and Ph) with the ligand precipitated in high yields when equimolar quantities of the reactants were mixed and refluxed for 2 h in dry ethanol. The complexes were recovered from the solution by filtration, followed by washing with ether and drying *in vacuo*, to give yellow powders.

TABLE I. Reaction Condition and Analytical Data

R_2SnCl_2	Ligand PT	Solvent	Compound	Reaction time (h)	Analysis (%)[a]				
					C	H	N	S	Cl
Me_2SnCl_2 0.55 g, 2 mmol	0.36g 2 mmol	EtOH	$Me_2Sn(PT)_2$ (I)	2	37.61 (37.87)	4.19 (3.94)	22.13 (22.09)	12.57 (12.62)	
Bu_2SnCl_2 0.61 g, 2 mmol	0.36g 2 mmol	EtOH	Bu_2SnCl_2PT (II)	2	37.17 (37.19)	5.37 (5.37)	12.12 (11.57)	6.42 (6.61)	14.45 (14.67)
Oct_2SnCl_2 0.84 g, 2 mmol	0.36g 2 mmol	EtOH	Oct_2SnCl_2PT (III)	2	45.72 (46.31)	6.82 (7.05)	9.34 (9.40)	5.42 (5.40)	11.68 (11.91)
Ph_2SnCl_2 0.69 g, 2 mmol	0.36g 2 mmol	EtOH	Ph_2SnCl_2PT (IV)	2	43.48 (43.59)	3.50 (3.44)	10.69 (10.70)	6.14 (6.12)	13.94 (13.88)

[a] Calculated values in parentheses.

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Instruments

Elemental analyses were determined using Perkin-Elmer Model 240 G Elemental analyser.

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

^{119m}Sn Mössbauer spectra were obtained using a constant acceleration spectrometer. The symmetrical triangular velocity drive waveform was derived from the multianalyser driven in the time mode by an external crystal controlled oscillator; 512 channels were used throughout. A ^{15}mCiCa^{119}SnO$_3$ source was used at room temperature, and the samples were packed in perspex discs and cooled to 80 K using a continuous-flow cryostat with nitrogen as the exchange gas. The spectrometer was calibrated using the magnetic splitting of an enriched ^{57}Fe absorber foil. The data were folded to determine the zero velocity position, and the folded data fitted with Loretzian functions by usual least-squares fitting techniques [10]. The non-linearity of the spectrometer was determined, by a free fit of the Fe data, to be less than +0.06%. The quoted experimental error of the +0.02 mm s^{-1} in the measured values of isomer shift and quadrupole splitting takes into account errors associated with non-linearities, calibration, zero velocity determination and computer fitting. The results are presented in Table II and a typical Mössbauer spectrum is shown in Fig. 1.

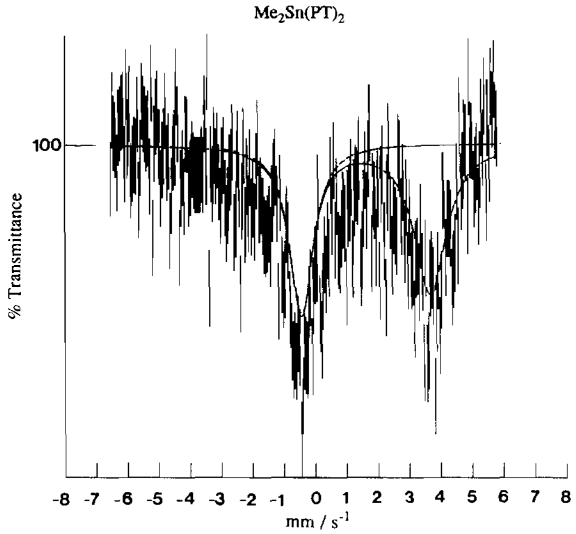


Fig. 1. Mössbauer spectrum of Me$_2$Sn(PT)$_2$.

TABLE II. Mössbauer Data for the Complexes

Complex	Isomer shift (mm s^{-1})	Quadrupole splitting (mm s^{-1})	Γ_1	Γ_2
Me$_2$Sn(PT)$_2$ (I)	1.78	4.12	0.920	1.238
Bu$_2$SnCl$_2$PT (II)	1.47	3.92	1.858	1.709
Oct$_2$SnCl$_2$PT (III)	1.40	3.81	1.179	1.066
Ph$_2$SnCl$_2$PT (IV)	1.38	3.74	1.049	1.000

Results and Discussion

Mössbauer Spectra

^{119}Sn isomer shifts (δ), quadrupole splittings (Δ_{E_q}) and the line widths, Γ_1 and Γ_2 for the complexes are summarized in Table II.

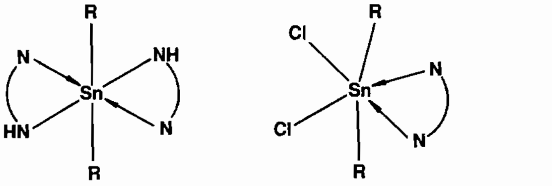
Isomer Shifts

The isomer shift values lie within the range 1.38–1.78 mm s^{-1}. They are more positive than for some complexes with oxygen, sulphur and nitrogen donors [11–13] indicating a higher s-electron density at the tin centre. It is clear from this work and from others [13] that isomer shift is a sensitive probe for the strength of an interaction between Sn(IV) and a Lewis base. A high positive δ value suggests a relatively weak interaction of Sn(IV) with nitrogen in agreement with the predominant class (A) character of Sn(IV). Furthermore δ values equal to or greater than 0.80 mm s^{-1} infer an s-electron density at the tin nucleus similar to that in SnCl$_4$ [11].

In order to invoke less d-orbital participation in explaining the convectional sp^{3}d^2 hybridization accorded to octahedral geometries, the Sn 5s electron density in the Sn–N bonds will have the overall effects of leaving a greater proportion of s-electron density at the tin centre since nitrogen is considerably less electronegative than chlorine. Thus the tin will have predominantly more 5s and less 5p character used in bonding to nitrogen and vice versa for bonding to chlorine.

Quadrupole Splitting

A great deal of effort has been devoted to the interpretation of quadrupole splittings in hexacoordinated Sn(IV) complexes. Yeats and his coworkers [13] concluded from studies on oxygen complexes of SnCl$_4$ that, in the presence of weak interaction between donor and acceptor, steric and structural effects are the principal origin of the magnitude of the quadrupole splitting. Furthermore, the quadrupole splitting is sensitive to *cis–trans*-isomerism in hexacoordinated diorganotin compounds, with the *trans*-isomer exhibiting the larger splitting [14]. Fortunately for the nitrogen complexes examined in this work, discussion of factors affecting Δ_{E_q} is not complicated by structural



I, R = Me   II, R = Bu; III, R = Oct; IV, R = Ph

Fig. 2. Structures I–IV.

isomerism since the vibrational data confirmed a *trans* configuration for the organic groups in these complexes. Hence all the complexes show large quadrupole splitting as expected on the basis of *trans*-R_2 only geometry around tin.

The largest Δ_{Eq} value (4.12 mm s^{-1}) is found for the $Me_2Sn(PT)_2$ complex consistent with a *trans* configuration in comformity with Bancroft [15] point charge approximation which predicts that quadrupole splitting for *trans*-dialkyl compounds decrease smoothly away from 4.0 mm s^{-1} for a regular octahedral geometry (∠CSnC 180°). Hence $Me_2Sn(PT)_2$ complex of Δ_{Eq} of 4.12 mm s^{-1} adopts a regular octahedral geometry Fig. 2 (**I**).

According to Bancroft, as the Δ_{Eq} decrease smoothly from 4.0 mm s^{-1}, the octahedral geometry becomes more distorted (*i.e.* ∠CSnC is less than 180°). Hence the three dialkyl complexes R_2SnCl_2PT (where R = Bu, Oct and Ph) with Δ_{Eq} values which decrease smoothly from 4.0 mm s^{-1}, exhibit quadrupole splittings consistent with a distorted octahedral *trans* configuration [15, 16] with both the ring nitrogen and the NH_2 moieties of the PT ligand coordinated to the tin centre (Fig. 2: **II**, **III**, **IV**).

Vibrational Spectra

The spectra of the uncomplexed ligand and the complexes together with assignments are summarized in Table III. The highest frequency band of the uncomplexed ligand centred at 3425 cm^{-1} is attributable to the unsymmetric ν(N–H) stretching vibration of the terminal NH_2 group [3] while the other bands at 3250 and 3140 cm^{-1} are due to the symmetric ν(N–H) vibrations of the imino and amino groups. The C=C and C=N stretching vibrations are overlapping and the band at 1618 cm^{-1} (doublet) is assigned to them. The band centred at 1585 cm^{-1} is ascribed to δ(N–H) vibration of the NH_2 group [17]. The band at 780 cm^{-1} is assigned to ν(C=S) and ν(C–N) modes [18]. The bands at 610 and 423 cm^{-1} in the free ligand are assigned to in-plane pyridine ring deformation and out-of-plane ring deformation, respectively [19].

The spectra of compound **I**, $Me_2Sn(PT)_2$, deserves comment. In this compound the bands due to both unsymmetric and symmetric stretching vibrations of the terminal NH_2 moiety in the free ligand have disappeared with the implication that there is substitution at that end. Thus the band at 3140 cm^{-1} in this compound is assigned to the ν(N–H) stretching frequency. Another interesting feature of the spectra of this compound is again the complete disappearance of the δ(N–H) deformation of the NH_2 group prominent at 1585 cm^{-1} in the free ligand. This can only suggest the absence of the NH_2 group in compound **I**. The band at 780 cm^{-1} due to ν(C=S) and ν(C–N) vibrations in the uncomplexed ligand remains unshifted in $Me_2Sn(PT)_2$ with the implication that the enol form of C=S is not involved in the bonding. The bands in the range 356 to 361 cm^{-1} which are not present in the free ligand have been tentatively assigned to the ν(Sn–N) vibration.

In the other complexes, there are considerable changes in the NH_2 group vibrations with the implication that the nitrogen of the terminal NH_2 is involved in complex formation. Both the unsymmetric and symmetric (N–H) stretching vibrations have shifted to higher frequencies. Also in these complexes, the δ(N–H) deformation of the NH_2 group is shifted because the nitrogen is involved in bonding. The prominent band at 780 cm^{-1} in the uncomplexed ligand remains unchanged, implying

TABLE III. Selected Infrared Spectra of PT and the Complexes

PT	$Me_2Sn(PT)_2$	Bu_2SnCl_2PT	Oct_2SnCl_2PT	Ph_2SnCl_2PT	Assignments
3425		3422	3424	3420	ν_{asy}(N–H)
3250		3245	3247	3245	ν_{sym}(N–H)
3140	3142	3141	3142	3143	ν(N–H)
1618	1618	1618	1618	1618	ν(C=N)
1585	–	1588	1588	1590	δ(N–H) of NH_2
780	780	780	780	780	ν(C=S) + ν(C–N)
610	628	629	630	630	i.p.def pyridine ring
423	437	436	436	435	o.p.def pyridine ring
	356	358	361	360	ν(Sn–N)?
		254	252	255	ν_{asy}(Sn–Cl)
		246	248	245	ν_{sym}(Sn–Cl)

as before that the enolised form of C=S is not involved in bonding. The in-plane and out-of-plane pyridine ring modes have moved to higher wave numbers with the implication that the ring nitrogen is involved in complex formation.

In the far infrared region, the diorganotin complexes exhibit bands in the regions 252–255 and 245–248 cm^{-1} which are absent in the spectra of the ligand and the organotin chlorides. These are ascribed to ν_{asy}(Sn–Cl) and ν_{sym}(Sn–Cl), respectively in excellent agreement with values reported for similar dialkyl chelate complexes [20, 21] for which *cis* halogen structures have been crystallographically demonstrated [22, 23].

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