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COMPLEX FORMATION BETWEEN ORGANOTIN CHLORIDES AND 2-AMINOMETHYL- AND 2-(2'-AMINOETHYL)-PYRIDINE

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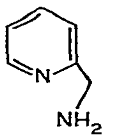
Summary

The complex formation between organotin chlorides and the potentially bidentate ligands, 2-aminomethylpyridine (AMP) and 2-(2'-aminoethyl)pyridine (AEP), has been investigated. In all cases, adducts with a 1/1 stoichiometry are formed and their solid state configurations have been studied by ^{119m}Sn Mössbauer and far infrared spectroscopy. The AMP ligand functions as a bidentate donor towards mono- and di-organotin chlorides to form octahedral complexes, whereas, in the adduct of triphenyltin chloride with AMP, the tin atom is five coordinate and the AMP ligand monodentate. The AEP ligand shows a much reduced tendency to complex the organotin chlorides.

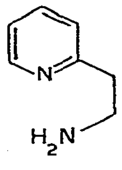
Introduction

There are few reports on the coordination complexes of primary amines with organotin halides. Isolable adducts appear to have been obtained largely with aniline and benzylamine [1], while evidence of coordination in solution has also been described in a few cases [2]. More recent examples of complexation include the 1/1 adducts of trimethyltin chloride with ethylenediamine [3] and of diphenyltin dichloride with 2-aminobenzthiazole [4], for which five- and six-fold coordination at tin have been suggested, respectively. Pentacoordinate tin has also been established for trimethyltin glycinate [5], which has a polymeric structure consisting of planar trimethyltin units linked by bridging NH_2 groups.

In view of our recent observation [6] of anti-tumour activity among hexacovalent complexes of diorganotin dihalides and pseudohalides with certain bidentate N-donor ligands, it was of interest to synthesis several new and related complexes within this class and investigate their activity. We describe in this paper the reactions of a range of organotin chlorides with 2-aminomethylpyridine (AMP; I) and 2-(2′-aminoethyl)pyridine (AEP; II):



(I)



(II)

II has previously been shown [7] to function as a bidentate ligand towards both platinum(II) and palladium(II) halides, yielding square planar complexes of formula, M(AEP)X_2.

Experimental

Synthesis of complexes

(a) With diorganotin dichlorides. 1/1 adducts of the diorganotin dichlorides, R_2SnCl_2 (R = Me, Et, Bu and Ph) with I and of dimethyl- and diphenyl-tin dichlorides with II precipitated in high yields when equimolar quantities of the reactants were mixed in dry ether. The complexes were recovered from the solution by filtration, followed by washing with ether and drying in vacuo, to give white or off-white powders. The two diorganotin dichloride adducts of AEP were found to be extremely hygroscopic.

(b) With mono-organotin trichlorides. 1/1 complexes of butyl- and phenyltin trichlorides with I were prepared by mixing equimolar quantities of the reactants in methanol and allowing the product to crystallise at room temperature. Phenyltin trichloride also formed a 1/1 adduct with II, but ether was used as the solvent in this case, since the complex could not be prepared in methanol.

(c) With triphenyltin chloride. The 1/1 adduct of triphenyltin chloride with I was precipitated when equimolar quantities of the reactants were mixed in ether and was recrystallised from the same solvent as white needles. If methanol was used as the solvent, only triphenyltin hydroxide could be recovered. The reaction of triphenyltin chloride with II in methanol yielded the hygroscopic salt, 2-(2′-aminoethyl)-pyridinium hydrochloride, m.p. 117—118°C (Found: C. 52.13; H, 6.82; N, 17.19, $C_7H_{11}N_2Cl$ calcd.: C, 52.99; H, 6.94; N, 17.66%) obtained upon concentrating the solution and adding ether.

The melting point and analytical data for the new complexes are recorded in Table 1.

Reaction of diorganotin dichlorides with I and II in methanol

Equimolar quantities of the diorganotin dichlorides, R_2SnCl_2 (R = Me, Bu, Oct, Ph and $PhCH_2$) and I were mixed in methanol at room temperature and, on standing for a few minutes, white crystalline precipitates of the tetraorgano-

TABLE 1

ANALYTICAL DATA FOR ORGANOTIN CHLORIDE ADDUCTS WITH AMP AND AEP.

Complex		Found	(Calcd.)	(%)	M.P.
	C	H	N	Cl	(°C)
Ph_3SnCl, AMP	57.80	4.80	5.75	7.27	114—116
	(58.36)	(4.66)	(5.67)	(7.19)	
Me_2SnCl_2, AMP	29.31	4.50	8.53	21.15	190—192
	(29.27)	(4.27)	(8.54)	(21.65)	
Et_2SnCl_2, AMP	33.71	5.06	7.87	19.94	157—159 (d.)
	(34.19)	(5.03)	(8.37)	(20.70)	
Bu_2SnCl_2, AMP	39.78	6.24	7.66	17.87	103—106
	(40.78)	(6.31)	(6.80)	(17.23)	
Ph_2SnCl, AMP	47.54	4.05	6.89	14.73	190—192
	(47.79)	(3.98)	(6.19)	(15.71)	
$BuSnCl_3$, AMP	30.85	4.39	7.19	27.37	227—228 (d.)
	(30.77)	(4.39)	(7.18)	(27.25)	
$PhSnCl_3$, AMP	34.96	3.15	6.82	26.03	222 (d.)
	(35.13)	(3.19)	(6.83)	(25.92)	
$PhSnCl_3$, AEP	35.96	3.93	6.59	24.65	192—195 (d.)
	(36.80)	(3.65)	(6.60)	(25.07)	
Me_2SnCl_2, AEP [a]	32.45	5.09	8.67	[b]	162—163 (d.)
	(31.61)	(4.68)	(8.19)	(20.76)	
Ph_2SnCl_2, AEP · H_2O [a]	47.04	4.59	6.19	[b]	120—122 (d.)
	(47.10)	(4.54)	(5.78)	(14.67)	

[a] Hygroscopic.
[b] Not performed.

TABLE 2

ANALYTICAL DATA FOR THE DISTANNOXANES $ClR_2SnOSnR_2OMe$

R	Analysis (Found(calcd.)(%))			M.p. (°C)
	C	H	Cl	
Me	15.58	3.94	9.12	>300
	(15.77)	(3.94)	(9.20)	(~200) [a]
Bu	36.07	7.05	7.36	72—75
	(37.19)	(7.11)	(6.47)	
Oct	51.07	9.07	4.70	54—56
	(51.26)	(9.07)	(4.53)	
Ph	46.85	3.46	5.63	236
	(47.73)	(3.66)	(5.65)	
CH_2Ph	50.36	4.53	5.86	150
	(50.84)	(4.53)	(5.19)	

[a] Ref. 8.

1-chloro-3-methoxydistannoxanes, $ClR_2SnOSnR_2OMe$, were formed. In agreement with earlier work on related derivatives [8], the stability of these compounds was found to decrease with increasing alkyl chain length. The melting points and analytical data are shown in Table 2.

The reactions of the diorganotin dichlorides R_2SnCl_2 (R = Me, Et or Ph) with equimolar quantities of II in methanol yielded the symmetrical tetraorgano-1,3-dichlorodistannoxanes, $(ClR_2Sn)_2O$.

Mössbauer spectra

^{119m}Sn Mössbauer spectra were obtained using a constant acceleration spectrometer, the symmetrical triangular velocity drive waveform being derived from the multichannel analyser driven in the time mode by an external crystal controlled oscillator; 512 channels were used throughout. A 15 mCi $Ca^{119}SnO_3$ 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 helium 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 Lorentzian functions by a least squares fitting programme [9]. 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 ±0.02 mm sec^{-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 reported in Table 3 and a typical Mössbauer spectrum is shown in Fig. 1.

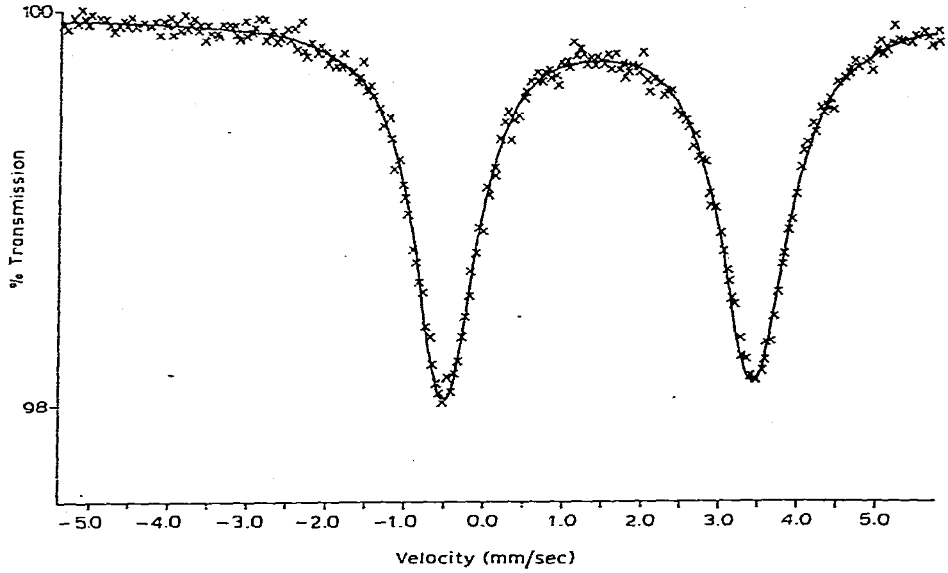


Fig. 1. ^{119m}Sn Mössbauer spectrum of Me_2SnCl_2AMP at 80 K.

TABLE 3

^{119m}Sn MÖSSBAUER DATA AT 80K

Complex	δ [a] (mm s^{-1})	ΔE_Q (mm s^{-1})
$Ph_3SnClAMP$	1.27	2.89
Ph_3SnClpiperidine [b]	1.25	2.95
Me_2SnCl_2AMP	1.34	3.72
Et_2SnCl_2AMP	1.54	3.78
Bu_2SnCl_2AMP	1.38	3.22
Ph_2SnCl_2AMP	0.95	2.17
$Ph_2Sn(NCS)_2$bipy [c]	0.82	2.13
$Bu_2Sn(NCS)_2$bipy [c]	1.43	4.04
$BuSnCl_3AMP$	1.00	1.95
$PhSnCl_3AMP$	0.87	1.85
$PhSnCl_3AEP$	0.81	1.82

[a] Rel. to $CaSnO_3$. [b] Ref. 10, [c] Ref. 11.

Infrared spectra

Far infrared spectra were obtained on Grubb Parsons DM4 or Perkin—Elmer 225 spectrometers using nujol mulls and CsI or polythene discs.

Discussion

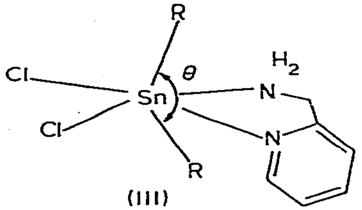
The Mössbauer isomer shift (δ) and quadrupole splitting (ΔE_Q) parameters observed for Ph_3SnCl,AMP (Table 3) compare favourably with those reported [10] for the 1/1 adducts of triphenyltin chloride with piperidine and isoquinoline, which have trigonal bipyramidal structures with essentially planar Ph_3Sn moieties. This suggests that a similar configuration at tin also prevails in Ph_3SnCl,AMP. Indeed, examples of 6-coordinate complexes of triorganotin halides with bidentate donor ligands are rare [12,13] and none have yet been demonstrated crystallographically [14]. Using the point charge model, the partial quadrupole splitting of a monodentate AMP ligand occupying the axial position of a trigonal bipyramid, $(pqs)^{tba}_{AMP}$, may be calculated [15] from eqn. 1:

$$\Delta E_Q(\mathrm{obs}) = -2(pqs)^{tba}_{Cl} + 2(pqs)^{tba}_{AMP} - 3(pqs)^{tbe}_{Ph} \qquad (1)$$

where $(pqs)^{tba}_{Cl} = 0.00$ mm sec^{-1}, $(pqs)^{tbe}_{Ph} = -0.98$ mm sec^{-1} and $\Delta E_Q(\mathrm{obs}) = 2.89$ mm sec^{-1} (Table 3).

The derived value for $(pqs)^{tba}_{AMP}$ of -0.025 mm sec^{-1} compares favourably with that of -0.035 mm sec^{-1} reported [15] for the ligand pyridine in the axial position, $(pqs)^{tba}_{py}$, and suggests that, in the AMP complex, the ring nitrogen is the donor atom.

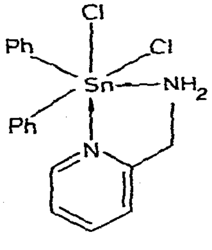
The three dialkyltin complexes, R_2SnCl_2,AMP (where R = Me, Et or Bu), show ΔE_Q values which are consistent with a distorted octahedral *trans*-$R_2SnX_2L_2$ configuration [16,17] with both the ring nitrogen and the NH_2 group of the AMP ligand coordinated to the tin atom (III):



(III)

In the far infrared region, the diorganotin complexes show bands at 254 and 248 cm^{-1} which are absent in the spectra of the ligand and the organotin dichlorides. These are assigned to $\nu_{sym}(Sn{-}Cl)$ and $\nu_{asym}(Sn{-}Cl)$, respectively, and are in excellent agreement with the values reported for a number of dialkyl- and diphenyl-tin dichloride chelate complexes [18—20] for which *cis*-halogen structures have been strongly inferred or demonstrated crystallographically [21—23].

Using the point charge approximation, Bancroft [17] has shown that the quadrupole splittings for trans-dialkyltin compounds decrease smoothly away from 4 mm sec^{-1} for a regular octahedral geometry (θ 180°) as the structure becomes more distorted, *i.e.* θ becomes less than 180°. The ΔE_Q values observed for Me_2SnCl_2AMP and Et_2SnCl_2AMP indicate a CSnC bond angle of $\approx$160° and for Bu_2SnCl_2AMP of $\approx$140°. Using a value of ΔE_Q 3.78 mm s^{-1}, a pqs of -0.17 mm s^{-1} may be derived for the AMP ligand by the point-charge equation appropriate to structure III [24]. This, in turn, may be used to estimate ΔE_Q for Ph_2SnCl_2AMP. The calculated value for structure III is 3.46 mm s^{-1}. The observed value, however (Table 3), is indicative [16,17] of a *cis*-octahedral chelate structure (IV) and is very close to the calculated ΔE_Q of 2.24 mm s^{-1}.

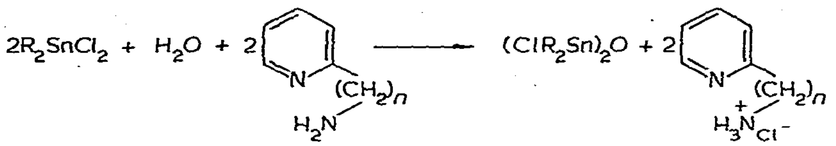


(IV)

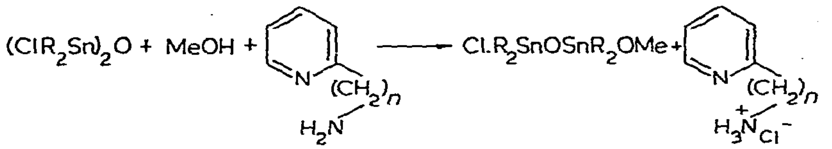
A similar change in configuration from *trans*-$(alkyl)_2SnX_2L_2$ to *cis*-$Ph_2SnX_2L_2$ is observed for [11,25] $(alkyl)_2Sn(NCS)_2L_2 \rightarrow Ph_2Sn(NCS)_2L_2$ but not for [25,26] $(alkyl)_2SnCl_2L_2 \rightarrow Ph_2SnCl_2L_2$, where L_2 = 2,2'-bipyridine or 1,10-phenanthroline (see also Table 3). The reasons for this interesting change of geometry are not clear but Parish [27] has suggested that, since all *cis*-$R_2SnX_2L_2$ complexes involve at least one chelating ligand and the majority are diphenyltin adducts, steric effects may be responsible for the *cis*-configuration.

The quadrupole splitting values obtained for the complexes of $BuSnCl_3$ and $PhSnCl_3$ (Table 3) compare favourably with the data of Barbieri et al. [28] for the octahedral bipyridyl and phenanthroline adducts of these trihalides.

Our attempts to prepare the complexes in protic solvents, such as methanol, were generally unsuccessful (see Experimental) and, in the case of the diorganotin dichlorides R_2SnCl_2 (where R = Me, Et, Bu, Ph or $PhCH_2$), the products isolated were either the tetraorgano-1-chloro-3-methyoxydistannoxanes (Table 2) or the tetraorgano-1,3-dichlorodistannoxanes. In this case, partial hydrolysis of the R_2SnCl_2 compound in the alcoholic solvent, induced by the organic base (I or II), to the tetraorgano-1,3-dichlorodistannoxane [29] has occurred (eq. 2), followed by partial alcoholysis of the latter [8] to give the tetraorgano-1-chloro-3-methoxydistannoxanes (eq. 3; n = 1 or 2):



(2)



(3)

This was found to be a very convenient method for preparing the tetraorgano-1-chloro-3-methoxydistannoxanes.

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