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## Preparation and $^{119m}\text{Sn}$ Mössbauer studies of diorganotin(IV) derivatives of nicotinic acid and nicotinic acid *N*-oxide

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### Abstract

Sixteen complexes of nicotinic acid and nicotinic acid *N*-oxide have been prepared with diorganotin(IV) oxides in 1:1 and 2:1 (ligand:metal) molar ratio. Formulae of diorganotin nicotinate are (i)  $\text{R}_2\text{Sn}(\text{Nic})_2$  [2:1] and (ii)  $[\text{R}_2\text{SnNic}]_2\text{O}$  [1:1] and of diorganotin nicotinate *N*-oxides are (iii)  $\text{R}_2\text{Sn}(\text{NicO})_2$  [2:1] and (iv)  $[\text{R}_2\text{SnNicO}]_2\text{O}$  [1:1] ( $\text{R} = \text{CH}_3$ ,  $^n\text{C}_4\text{H}_9$ ,  $^{13}\text{C}_8\text{H}_{17}$ ,  $\text{C}_6\text{H}_5\text{CH}_2$ ; Nic = anion of nicotinic acid, NicO = anion of nicotinic acid *N*-oxide). All the butyl- and octyltin derivatives are monomeric and are more soluble whereas dimethyl- and dibenzyltin derivatives are polymers and are less soluble or insoluble in common solvents. Mössbauer,  $^1\text{H}$  NMR and IR spectral studies have been used to assign structures. All the 2:1 complexes possess distorted *trans* octahedral and all the 1:1 complexes of nicotinic acid have five coordinate distorted *trans* trigonal bipyramidal structures. However, the 1:1 dinuclear complexes of nicotinic acid *N*-oxide contain a six coordinated and a five coordinated tin(IV) in the same molecule. A Sn–O–Sn bridged structure is present in all the 1:1 complexes. Unlike analogous picolinic acid complexes there is no coordination from ring nitrogen to tin(IV). The carboxylate group is bidentate in all the nicotinic acid complexes whereas it is unidentate in all the picolinic acid complexes as we showed in *J. Organomet. Chem.*, 411 (1991) 89.

### Introduction

Only few triorgano- and diorganotin(IV) nicotinate have been reported [2,3]. Our interest in this communication is to report preparation and structure elucidation studies of diorganotin(IV) complexes with nicotinic acid and nicotinic acid *N*-oxide.

### Experimental section

All the diorganotin oxides were procured from Alfa Inorganics and used as such. Nicotinic acid and nicotinic acid *N*-oxide were obtained from Aldrich Chemicals and also used as such.

### Physical measurements

Elemental analyses were carried out by Microanalytical Service, Calcutta University, Calcutta. Tin was estimated as  $\text{SnO}_2$ . Molecular weight determinations were

Table 1  
Analytical and physical data of the complexes of NicH/NicOH

Compound	Colour	Yield (%)	M.p. (°C)	Analysis (Found (calc.) (%))			Mol. Wt. found (calc.)	Molecular complexity <sup>c</sup>
				C	H	N		
(1) $(\text{CH}_3)_2\text{Sn}(\text{Nic})_2^a$	White	65	277-278	42.36 (42.96)	3.35 (3.57)	7.62 (7.14)	<sup>d</sup> 30.55 (30.23)	P
(2) $(^n\text{C}_4\text{H}_9)_2\text{Sn}(\text{Nic})_2^b$	White	70	140-141	50.30 (50.36)	5.49 (5.63)	6.40 (5.90)	525 (476)	M
(3) $(^n\text{C}_8\text{H}_{17})_2\text{Sn}(\text{Nic})_2^b$	Off-white	63	104-106	57.64 (58.04)	7.92 (7.10)	4.63 (4.75)	545 (588)	M
(4) $(\text{C}_8\text{H}_5\text{CH}_2)_2\text{Sn}(\text{Nic})_2^a$	Flesh	72	275-276	-	4.13 (4.04)	4.70 (5.15)	<sup>d</sup> 21.09 (21.79)	P
(5) $[(\text{CH}_3)_2\text{Sn}(\text{Nic})]_2\text{O}^a$	White	67	271-273	34.75 (34.42)	3.36 (3.45)	5.38 (5.20)	<sup>d</sup> 42.15 (42.59)	P
(6) $[(^n\text{C}_4\text{H}_9)_2\text{Sn}(\text{Nic})]_2\text{O}^b$	Yellowish white	75	119-120	46.07 (46.32)	6.35 (6.25)	4.06 (3.76)	780 (724)	M
(7) $[(^n\text{C}_8\text{H}_{17})_2\text{Sn}(\text{Nic})]_2\text{O}^b$	Pale yellow	60	Semi-solid	53.82 (54.76)	8.28 (8.25)	2.98 (2.95)	933 (948)	M
(8) $[(\text{C}_8\text{H}_5\text{CH}_2)_2\text{Sn}(\text{Nic})]_2\text{O}^a$	Flesh	69	259-260	57.64 (57.07)	7.92 (7.19)	5.62 (4.76)	<sup>d</sup> 26.99 (27.56)	P

(9)	$(\text{CH}_3)_2\text{Sn}(\text{NicO})_2^a$	White	55	246–249	40.66 (39.62)	3.51 (3.30)	6.80 (6.60)	27.37 (27.99)	<sup>d</sup>	P
(10)	$(^{13}\text{C}_4\text{H}_9)_2\text{Sn}(\text{NicO})_2^b$	White	60	191–194	47.14 (47.24)	4.98 (5.12)	5.35 (5.51)	23.36 (23.37)	503 (508)	M
(11)	$(^{13}\text{C}_8\text{H}_{17})_2\text{Sn}(\text{NicO})_2^b$	Off-white	64	188–190	55.29 (54.49)	6.80 (6.77)	4.74 (4.52)	18.95 (19.15)	538 (620)	M
(12)	$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Sn}(\text{NicO})_2^a$	Off-white	72	225–229	–	4.13 (4.24)	4.70 (5.25)	21.07 (20.61)	<sup>d</sup>	P
(13)	$[(\text{CH}_3)_2\text{Sn}(\text{NicO})]_5\text{O}^a$	White	65	266–270	32.31 (32.65)	3.18 (3.40)	4.05 (4.76)	39.38 (39.37)	<sup>d</sup>	P
(14)	$[(^{13}\text{C}_4\text{H}_9)_2\text{Sn}(\text{NicO})]_2\text{O}^b$	White	54	181–184	44.05 (44.44)	6.28 (5.82)	4.09 (3.70)	30.88 (31.40)	686 (756)	M
(15)	$[(^{13}\text{C}_8\text{H}_{17})_2\text{Sn}(\text{NicO})]_2\text{O}^b$	White	59	173–176	54.01 (54.80)	7.96 (7.76)	3.08 (2.86)	24.14 (24.22)	893 (980)	M
(16)	$[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Sn}(\text{NicO})]_2\text{O}^a$	Off-white	60	237–240	56.22 (55.81)	4.67 (4.19)	3.76 (3.26)	27.19 (26.51)	<sup>d</sup>	P

<sup>a</sup> Crystallized or washed with hot 1 : 1 mixture of methanol and ethanol. <sup>b</sup> Crystallized from methanol/ethanol. <sup>c</sup> M = monomer, P = polymer. <sup>d</sup> Insoluble in camphor.

Table 2  
Infrared data of NiCH/NicOH complexes <sup>a</sup>

	Compound	$\nu(\text{COO})_{\text{asym}}$	$\nu(\text{COO})_{\text{sym}}$	$\Delta\nu$	$\nu(\text{N} \rightarrow \text{O})$	$\nu(\text{Sn}-\text{C})$	$\nu(\text{Sn}-\text{O})$	$\nu(\text{Sn}-\text{O}-\text{Sn})$
	NiCH	1710s	1325s	385	-	-	-	-
	Na-Nic	1615b	1375bs	240	-	-	-	-
(1)	$(\text{CH}_3)_2\text{Sn}(\text{Nic})_2$	1605s	1398s	207	-	520m	435s	-
(2)	$({}^n\text{C}_4\text{H}_9)_2\text{Sn}(\text{Nic})_2$	1610s	1410s	200	-	590m	430s	-
(3)	$({}^n\text{C}_8\text{H}_{17})_2\text{Sn}(\text{Nic})_2$	1610sh	1400s	210	-	520m	391sh	-
						600sh	545bw	-
(4)	$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Sn}(\text{Nic})_2$	1610w	1400sh	210	-	455m	495m	-
(5)	$[(\text{CH}_3)_2\text{Sn}(\text{Nic})]_2\text{O}$	1605s	1400s	205	-	520w	570-550bm	630
(6)	$[({}^n\text{C}_4\text{H}_9)_2\text{Sn}(\text{Nic})]_2\text{O}$	1605s	1400s	205	-	500m	485s	680s
(7)	$[({}^n\text{C}_8\text{H}_{17})_2\text{Sn}(\text{Nic})]_2\text{O}$	1610sh	1395bs	215	-	600sh	395sh	690s
						545b	550w	495s
(8)	$[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Sn}(\text{Nic})]_2\text{O}$	1605sh	1410s	195	-	600m	480s	600sh
						452m	430sh	-
	NicOH	1705s	1330s	375	1225bs	-	-	-
	Na-NicO	1615bs	1380bs	235	1240s	-	-	-
					1225s			

(9)	$(\text{CH}_3)_2\text{Sn}(\text{NicO})_2$	1650s	1355s	295	1220s 1190m	540w	465s 430w 335m 460s 300m 462s 335m 465s 340w 460s 345m 455m 335m 460m 339m 460m 350m	-
(10)	$(^n\text{C}_4\text{H}_9)_2\text{Sn}(\text{NicO})_2$	1640s	1360s	280	1215s 1190m	580m		-
(11)	$(^n\text{C}_8\text{H}_{17})_2\text{Sn}(\text{NicO})_2$	1640s	1350s	290	1215s 1190m	579m		-
(12)	$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Sn}(\text{NicO})_2$	1605s	1370s	280	1215s 1190m	435m 400w		-
(13)	$[(\text{CH}_3)_2\text{Sn}(\text{NicO})]_2\text{O}$	1645s	1355s	290	1215s 1185m	555m 520w		705m
(14)	$[(^n\text{C}_4\text{H}_9)_2\text{Sn}(\text{NicO})]_2\text{O}$	1640s	1350s	290	1215m 1185m	600sh		675s
(15)	$[(^n\text{C}_8\text{H}_{17})_2\text{Sn}(\text{NicO})]_2\text{O}$	1650s	1350s	300	1215s 1190m	600sh 555sh		670s
(16)	$[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Sn}(\text{NicO})]_2\text{O}$	1650s	1365s	285	1215s 1185m	435m 400wb		675m

<sup>a</sup> NicH = nicotinic acid, Na-Nic = Sodium salt of nicotinic acid, NicOH = Nicotinic acid, N-oxide, Na-NicO = Sodium salt of nicotinic acid N-oxide, s = strong, sh = shoulder, b = broad, w = weak, m = medium, bs = broad strong.  $\Delta\nu = \nu(\text{COO})_{\text{asym}} - \nu(\text{COO})_{\text{sym}}$ .

done by the Rast method (175 °C). Cryoscopic molecular weight determinations could not be carried out due to low solubility of the compounds at low temperature. Infrared spectra were recorded on Pye Unicam Spectrophotometer Sp<sub>3-300</sub> in 200–4000 cm<sup>-1</sup> range. <sup>1</sup>H NMR spectra were recorded on Tesla-BS-487C, 80 MHz using tetramethylsilane as the internal standard. Mössbauer spectra were recorded with a Harwell 6000 series spectrometer with samples cooled to 80 K and source (Pd–Sn) at room temperature. isomer shifts are relative to SnO<sub>2</sub> measured at room temperature.

#### *Preparation of the complexes*

The 1 : 1 and 2 : 1 diorganotin(IV) complexes of nicotinic acid and nicotinic acid *N*-oxide were prepared by dissolving nicotinic acid/nicotinic acid *N*-oxide, 0.001 mole and 0.002 mole, for 1 : 1 and 2 : 1 complexes respectively in dry thiophene free benzene (60 cm<sup>3</sup>) and adding to this solution diorganotin oxides (0.001 mole) in each case. The reaction mixture was refluxed on a water bath for about 4–5 h to give a clear solution in case of dibutyl- and dioctyltin complexes and a white solid in case of dimethyl- and dibenzyltin complexes. The soluble complexes were isolated by removing excess of benzene by distillation under reduced pressure and the insoluble complexes by filtration. Dibutyl- and dioctyltin complexes were recrystallized from dry methanol and dimethyl- and dibenzyltin complexes were crystallized or washed with a 1 : 1 mixture of methanol and ethanol.

#### **Results and discussion**

Complexes of nicotinic acid and nicotinic acid *N*-oxide have been prepared with diorganotin(IV) oxides in 1 : 1 and 2 : 1 molar ratio (ligand : metal). All 1 : 1 complexes are dinuclear with a Sn–O–Sn bridge. Dimethyl- and dibenzyltin compounds are less soluble in organic solvents and are polymeric in nature, whereas dibutyl- and dioctyltin derivatives are very soluble and are monomeric in nature. Physical and analytical data are given in Table 1. Molar conductance measurements in nitrobenzene show them to be non-electrolytes. The diorganotin(IV) nicotinate complexes have decreased solubility than the analogous picolinate complexes [1]. The structure elucidation studies have been carried out by infrared (Table 2, <sup>1</sup>H NMR (Table 3) and Mössbauer spectral data studies (Table 4).

#### *Infrared data*

Infrared spectra have been recorded in KBr in the solid state, and within the range 4000–200 cm<sup>-1</sup>. Important bands for structure assignment are  $\nu_{\text{asym}}(\text{COO})$ ,  $\nu_{\text{sym}}(\text{COO})$ ,  $\nu(\text{N} \rightarrow \text{O})$ ,  $\nu(\text{Sn}-\text{C})$ . In the nicotinic acid and nicotinic acid *N*-oxide, the  $\nu(\text{OH})$  of the COOH appear as broad bands in the range 2600–2200 cm<sup>-1</sup> and 2600–2400 cm<sup>-1</sup> respectively which disappear after complex formation thereby showing deprotonation of COOH group and reaction with diorganotin(IV). The mode of coordination of the carboxylate group is estimated from the difference ( $\Delta\nu$ ) in the  $\nu_{\text{asym}}(\text{COO})$  and  $\nu_{\text{sym}}(\text{COO})$  values and its comparison with that of respective sodium salts of the acids. In both types of nicotinic acid complexes  $\nu_{\text{asym}}(\text{COO})$  falls and  $\nu_{\text{sym}}(\text{COO})$  rises as compared to the  $\nu(\text{COO})$  values in the nicotinic acid and is in the range of sodium nicotinate  $\nu(\text{COO})$  values. The  $\Delta\nu$  values, 200–215 cm<sup>-1</sup> in case of the nicotinate complexes are also very closely comparable with that of the

Table 3

<sup>1</sup>H NMR data of NicH and NicOH complexes (scale – δ, ppm)

Compound <sup>a</sup>	Sn-R		-CH <sub>2</sub> -	-CH <sub>2</sub> Sn	Aromatic protons <sup>c</sup>			
	-CH <sub>3</sub>	-			H <sup>5</sup>	H <sup>4</sup>	H <sup>6</sup>	H <sup>2</sup>
NicH <sup>b</sup>	-	-	-	-	8.175 (m, 1H)	9.03-9.45 (m, 2H)	-	9.55 (s, 1H)
NicOH <sup>b</sup>	-	-	-	-	8.175 (m, 1H)	8.97 (d, 2H)	-	9.45 (s, 1H)
(2) ( <sup>n</sup> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(Nic) <sub>2</sub>	0.875 (t, 6H)	-	1.02-2.00 (m, 12H)	-	7.35 (m, 2H)	8.35 (m, 2H)	8.77 (m, 2H)	9.25 (m, 2H)
(3) ( <sup>n</sup> C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> Sn(Nic) <sub>2</sub>	0.825 (m, 6H)	-	1.20 (m, 24H)	1.80 (m, 4H)	7.37 (m, 2H)	8.37 (m, 2H)	8.77 (m, 2H)	9.15 (m, 2H)
(6) [( <sup>n</sup> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(Nic)] <sub>2</sub> O	0.875 (m, 12H)	-	1.15 (m, 16H)	1.80 (m, 8H)	7.35 (m, 2H)	8.25 (m, 2H)	8.70 (m, 2H)	9.17 (m, 2H)
(7) [( <sup>n</sup> C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> Sn(Nic)] <sub>2</sub> O	0.825 (m, 12H)	-	1.20 (m, 48H)	1.80 (m, 8H)	7.37 (m, 2H)	8.45 (m, 2H)	8.55 (m, 2H)	9.00 (m, 2H)
(10) ( <sup>n</sup> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(NicO) <sub>2</sub>	0.90 (m, 6H)	-	1.30 (m, 8H)	1.66 (m, 4H)	7.42 (m, 2H)	7.90-8.52 (m, 4H)	-	9.00 (m, 2H)
(11) ( <sup>n</sup> C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> Sn(NicO) <sub>2</sub>	0.80 (m, 6H)	-	1.17 (m, 24H)	1.65 (m, 4H)	7.42 (m, 2H)	7.90-8.52 (m, 4H)	-	9.00 (m, 2H)
(14) [( <sup>n</sup> C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn(NicO)] <sub>2</sub> O	0.93 (m, 12H)	-	1.07-1.95 (m, 24H)	-	7.30 (m, 2H)	7.95 (m, 2H)	8.30 (m, 2H)	8.75 (m, 2H)
(15) [( <sup>n</sup> C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> Sn(NicO)] <sub>2</sub> O	0.825 (m, 12H)	-	1.27 (m, 48H)	1.62 (m, 8H)	7.35 (m, 2H)	8.00 (m, 2H)	8.30 (m, 2H)	8.75 (m, 2H)

<sup>a</sup> All complexes are soluble in CDCl<sub>3</sub>. <sup>b</sup> In trifluoroacetic acid (TFA). <sup>c</sup> See text.

Table 4

Mössbauer data at 80 K ( $\text{mm s}^{-1}$ )

	Compound	IS	QS	Line widths		Expected structure
				1	2	
(2)	$(^{119}\text{C}_4\text{H}_9)_2\text{Sn}(\text{Nic})_2$	1.60	3.93	0.90	0.95	<i>trans</i> 6-coord.
(6)	$[(^{119}\text{C}_4\text{H}_9)_2\text{Sn}(\text{Nic})]_2\text{O}$	1.37	3.64	0.86	0.95	<i>trans</i> 5-coord.
(7)	$[(^{119}\text{C}_8\text{H}_{17})_2\text{Sn}(\text{Nic})]_2\text{O}$	1.30	3.35	0.94	1.00	<i>trans</i> 5-coord.
(9)	$(\text{CH}_3)_2\text{Sn}(\text{NicO})_2$	1.31	4.11	0.78	0.84	<i>trans</i> 6-coord.
(10)	$(^{119}\text{C}_4\text{H}_9)_2\text{Sn}(\text{NicO})_2$	1.46	4.17	0.97	0.92	<i>trans</i> 6-coord.
(11)	$(^{119}\text{C}_8\text{H}_{17})_2\text{Sn}(\text{NicO})_2$	1.42	4.04	0.93	0.85	<i>trans</i> 6-coord.
(13)	$[(\text{CH}_3)_2\text{Sn}(\text{NicO})]_2\text{O}$	1.30	4.19	0.79	0.81	<i>trans</i> 6-coord.
(14)	$[(^{119}\text{C}_4\text{H}_9)_2\text{Sn}(\text{NicO})]_2\text{O}$	0.94	2.15	0.87	0.86	<i>trans</i> 5-coord.
		1.40	4.26	0.72	0.86	<i>trans</i> 6-coord.
(15)	$[(^{119}\text{C}_8\text{H}_{17})_2\text{Sn}(\text{NicO})]_2\text{O}$	1.15	2.66	0.87	1.00	<i>trans</i> 5-coord.
		1.49	4.03	0.93	0.62	<i>trans</i> 6-coord.
		1.23	2.64	0.67	1.29	<i>trans</i> 5-coord.

sodium nicotinate ( $240 \text{ cm}^{-1}$ ). An intramolecular chelation of the carboxylate group to tin(IV) is present in the butyl- and octyltin nicotinic acid complexes whereas an intermolecular chelation is present in methyl- and benzyltin complexes. Thus the carboxylate group is bonded to tin(IV) in a bidentate manner in all the 1:1 and 2:1 complexes of nicotinic acid [4,5].

In the case of all the 1:1 and 2:1 complexes of nicotinic acid *N*-oxide the  $\nu_{\text{asym}}(\text{COO})$  falls and  $\nu_{\text{sym}}(\text{COO})$  rises as compared to the values in the case of the free acid and the  $\Delta\nu$  values are also lower in the case of the complexes. However, these values are higher than in the case of the sodium salt of nicotinic acid *N*-oxide and the difference in the  $\nu_{\text{asym}}(\text{COO})$  and  $\nu_{\text{sym}}(\text{COO})$  values ( $\Delta\nu = 280\text{--}300 \text{ cm}^{-1}$ ) in the case of the complexes is higher than that of the sodium salt of nicotinic acid *N*-oxide. Therefore, in the present series of nicotinic acid *N*-oxide complexes, the carboxylate group is bonded to tin(V) in a unidentate manner [1].

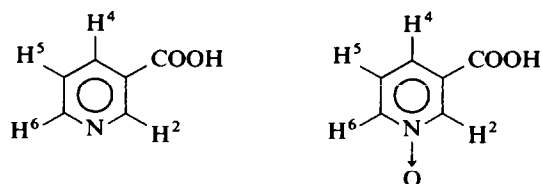
A broad strong band due to  $\nu(\text{N} \rightarrow \text{O})$  appears at  $1225 \text{ cm}^{-1}$  in the nicotinic acid *N*-oxide and as a split band in the form of two strong peaks at  $1240$  and  $1225 \text{ cm}^{-1}$  in the case of sodium salt of nicotinic acid *N*-oxide. In all the complexes two bands (one strong around  $1215$  and a medium band  $1185 \pm 5 \text{ cm}^{-1}$  with a difference of  $20 \pm 5 \text{ cm}^{-1}$ ) have been observed which are clearly due to two types of *N*-oxide oxygen bonding to tin(IV) to different extents [1]. In the case of monomeric 2:1 and 1:1 butyl- and octyltin nicotinate *N*-oxides the *N*-oxide oxygen is intramolecularly coordinated to form a part of a distorted octahedral or a distorted trigonal bipyramidal structure whereas in the case of dimethyl- and dibenzyltin nicotinate *N*-oxide the *N*-oxide oxygen exhibits intermolecular coordination. The presence of two  $\nu(\text{Sn}-\text{C})$  bands in the spectra of some complexes of both the acids in the region  $600\text{--}500 \text{ cm}^{-1}$  and  $455\text{--}430 \text{ cm}^{-1}$  regions indicates a *cis* position of the alkyl or aryl or a non-linear arrangement of R groups in a *trans* position. Presence of a single  $\nu(\text{Sn}-\text{C})$  band in some complexes points towards a linear or *trans* position of the R groups [6]. The identification of the  $\nu(\text{Sn}-\text{O})$  in the specified range ( $570\text{--}391 \text{ cm}^{-1}$  for nicotinic acid complexes and  $465\text{--}300 \text{ cm}^{-1}$  for the nicotinic acid *N*-oxide complexes) confirms coordination to tin(IV) from carboxylates of both the acids [6]. In case of the dinuclear 1:1 complexes of nicotinic acid and nicotinic acid *N*-oxide



a strong band in  $690\text{--}600\text{ cm}^{-1}$  and  $605\text{--}670\text{ cm}^{-1}$  region is assigned to the bridging Sn–O–Sn band respectively [5].

#### $^1\text{H}$ NMR spectra

The  $^1\text{H}$  NMR spectra of nicotinic acid and nicotinic acid *N*-oxide have been recorded in trifluoroacetic acid and of the soluble complexes in  $\text{CDCl}_3$  (Table 3).



The integrated area agrees with the total number of protons calculated from the expected molecular formula of the complexes of both the acids. The complex multiplet signals for alkyl and aryl Sn–R groups point to a non-linear position of the alkyl or aryl group in the five- or six-coordinate complexes. The signals due to all the four protons  $\text{H}^2$ ,  $\text{H}^4$ ,  $\text{H}^5$ ,  $\text{H}^6$  of the aromatic rings of the two acids experience an upfield shift after complex formation and the maximum upfield effect is on proton  $\text{H}^5$ .

#### Mössbauer spectra ( $\text{mm s}^{-1}$ )

Mössbauer parameters are helpful in determining the coordination number and the structure of the tin compounds. The isomer shift (IS) and quadrupole (QS) splitting values in the 2 : 1 complexes 2, 9, 10, 11 (IS, 1.31–1.61, QS 3.93–4.17) fall in the range of those noted for the *trans* octahedral complexes [8,4] since the *cis* arrangement of the R groups around tin(IV) leads to IS value below 1.0 [7]. In the case of 1 : 1 complexes of nicotinic acid 6 and 7, the IS and QS values (1.30, 1.37; 3.35, 3.64) fall in the range of five coordinated complexes [6] since the QS/IS ratio is greater than 2.0 which is generally associated with coordination number greater than four [8]. The 1 : 1 complexes of nicotinic acid *N*-oxide 13–15 show two types of environments for tin(IV) corresponding to a five coordinate and a six-coordinate geometry for tin(IV) since two sets of values of IS and QS have been observed.

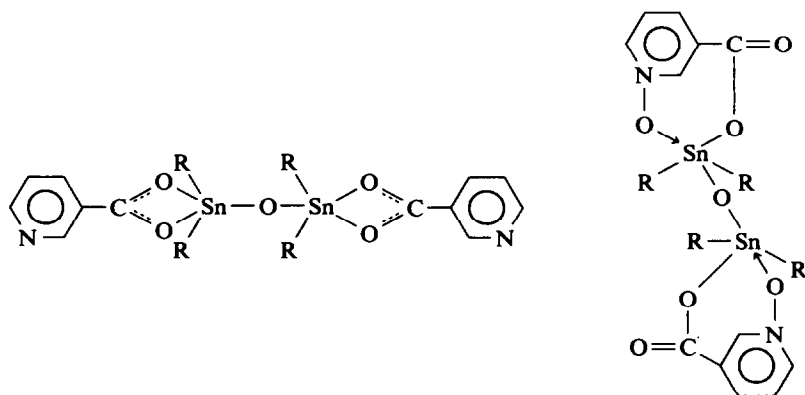


Fig. 1.  $\text{R} = {}^n\text{C}_4\text{H}_9$ ,  ${}^n\text{C}_8\text{H}_{17}$ .

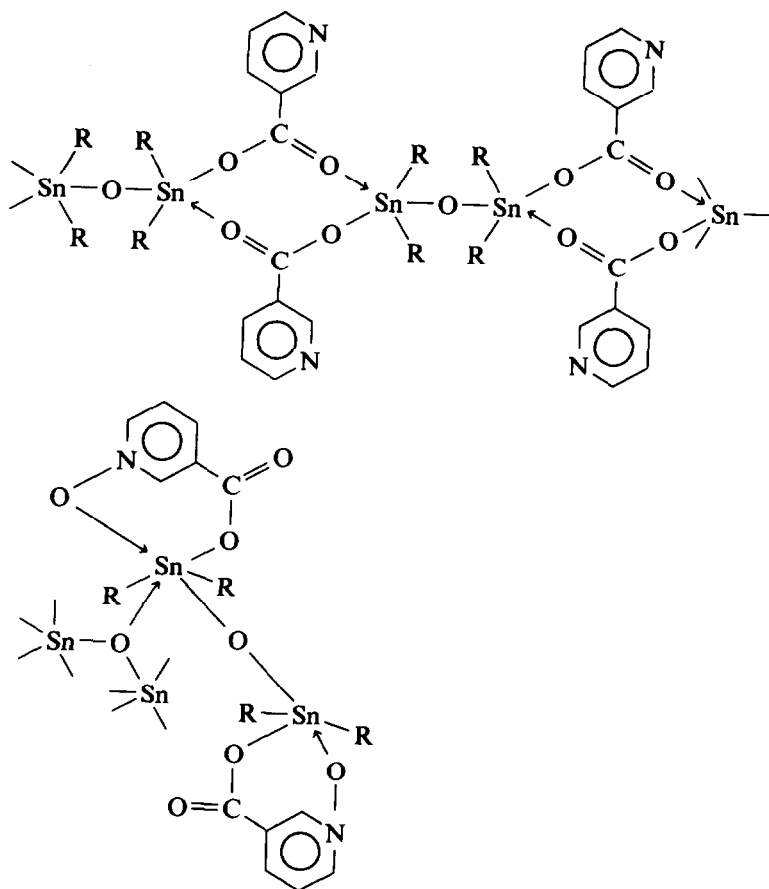


Fig. 2.  $R = CH_3, C_6H_5, CH_2$ .

These 1:1 complexes are dinuclear with Sn-O-Sn bridged structure in which six-coordinated tin is joined to a five-coordinated tin through an oxygen atom in the same molecule.

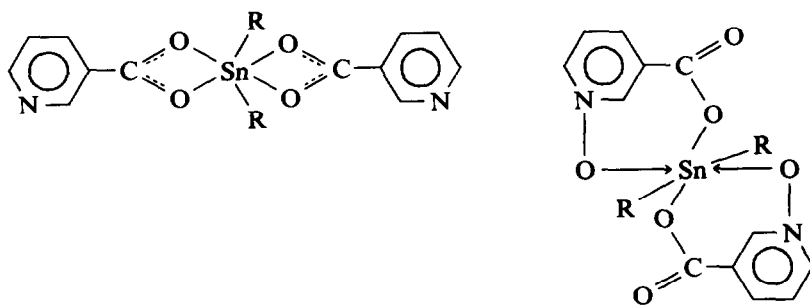


Fig. 3.  $R = {}^n C_4H_9, {}^n C_8H_{17}$ .

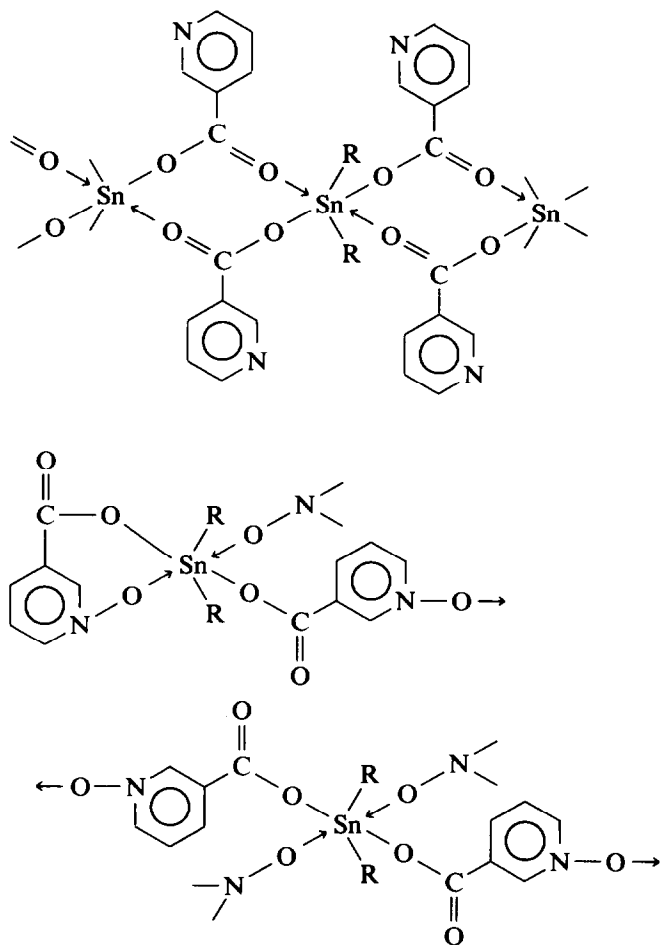


Fig. 4. R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>.

### Conclusion

The 1:1 complexes of nicotinic acid have five coordinate trigonal bipyramidal structures (Figs. 1 and 2) with a Sn–O–Sn bridge and a bidentate carboxylate group. However, the 1:1 dinuclear complexes of nicotinic acid *N*-oxide have a six-coordinated and a five-coordinated tin(IV) joined by a oxygen atom present in the same molecule (Fig. 2) [5]. These complexes are not mixtures of 1:1 or 2:1 complexes since elemental analysis does not tally with that. The spectral data support a non-linear configuration of the R–Sn–R moiety and distorted *trans* octahedral structures (Figs. 3 and 4) for all the 2:1 complexes.

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