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Preparation and ^{119m}Sn Mössbauer spectral studies of diorganotin(IV) derivatives of isonicotinic acid and isonicotinic acid N-oxide

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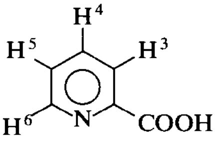
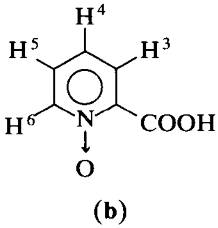
Abstract

The following new complexes, (i) $R_2Sn(^iNic)_2$ [1:2], (ii) $[R_2Sn^iNic]_2O$ [1:1], (iii) $R_2Sn(^iNicO)_2$ [1:2] and (iv) $[R_2Sn^iNicO]_2O$ [1:1] ($R = CH_3$, $^nC_4H_9$, $^nC_8H_{17}$, $C_6H_5CH_2$; ^{i}Nic = anion of isonicotinic acid, ^{i}NicO = anion of isonicotinic acid N-oxide), of isonicotinic acid and isonicotinic acid N-oxide have been prepared with diorganotin(IV) oxides in 1:1 and 2:1 ligand:metal molar ratio. Dibutyl- and dioctyltin(IV) complexes are more soluble than dimethyl- and dibenzyltin(IV) derivatives. IR, ^{1}H NMR and Mössbauer studies show all the 2:1 complexes to have a distorted *trans* octahedral and the 1:1 complexes a dinuclear trigonal bipyramidal structure with Sn–O–Sn bridge. However, the 1:1 complexes of isonicotinic acid N-oxide have present in the same molecule a six and a five coordinate tin(IV) atom, joined by an oxygen atom.

Introduction

In continuation of our earlier studies [1,2] we report here the preparation of some new diorganotin complexes of isonicotinic acid (**e**) and of the little-known [3] isonicotinic acid N-oxide (**f**) and describe their structures. It is very interesting to note that different bonding sites are present in complexes with the acids (**a**–**f**) illustrated below [1,2].


(a)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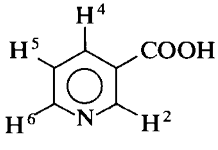
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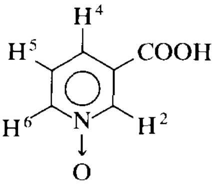

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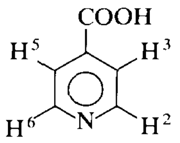
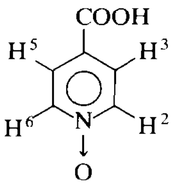


(e)



(f)

The following have been observed: unidentate carboxylates in complexes with **a** and **b**, a Sn–N bond in **a** and two N → O coordinated to tin; bidentate and unidentate carboxylates in complexes with **c** and **d** along with two N → O coordinated in **d**; asymmetrically bonded bidentate carboxylates in complexes with **e** and one unidentate and one bidentate carboxylate in all butyl and octyl complexes with **f** along with one coordinated and one free N → O; and finally, in all the methyl and benzyl derivatives with **f** two unidentate carboxylates and two coordinated N → O are present.

Experimental

Diorganotin oxides were used as obtained from Alfa Inorganics. Isonicotinic acid and isonicotinic acid N-oxide (Aldrich Chemicals) were used without further purification.

Physical measurements

Elemental analyses were carried out by the microanalytical service, University of Calcutta. Tin was estimated as SnO_2. Molecular weights were determined by the Rast method and could not be determined cryoscopically due to the reduced solubility of complexes at low temperature. Infrared spectra were recorded on a Pye Unicam Sp3-300 spectrophotometer. ^1H NMR spectra were recorded on a Tesla-BS-487C 80 MHz instrument. Mössbauer spectra were recorded on a Harwell 6000 series spectrometer with samples cooled by liquid nitrogen (80 K) and with the source (Pd–Sn) at room temperature. Isomer shifts are expressed relative to the SnO_2 measured at room temperature.

Preparation of complexes

The 1 : 1 and 2 : 1 ligand : metal complexes were prepared by dissolving isonicotinic acid or isonicotinic acid N-oxide (0.001 mole for 1 : 1 and 0.002 mole for 2 : 1) in thiophene free dry benzene (60 cm^3) to which was added diorganotin(IV) oxide (0.001 mole for 1 : 1 and 2 : 1). The contents were refluxed on a water bath using a Dean Stark trap for about 5–6 h. In the case of dibutyl and dioctyltin(IV) complexes a clear solution was obtained whereas in the cases of dimethyl- and dibenzyltin(IV) insoluble complexes were obtained. The solvent was removed from the soluble complexes by distillation under reduced pressure to leave a solid which was dried under vacuum. The insoluble complexes were separated by filtration. If soluble, complexes of isonicotinic acid N-oxide were crystallized from a 1 : 1 mixture of dry benzene and methanol; if insoluble, they were washed with one of the following 1 : 1 dry mixtures: benzene and methanol; benzene and ethanol; methanol and ethanol.

Results and discussion

Diorganotin(IV) complexes were prepared with isonicotinic acid and isonicotinic acid N-oxide in 1:1 and 2:1 ligand:metal molar ratio. Dibutyl- and dioctyltin(IV) complexes are soluble in common organic solvents whereas dimethyl- and dibenzyltin are less soluble. Dibutyl- and dioctyltin(IV) complexes are monomers whereas dimethyltin and dibenzyltin complexes are polymers, according to molecular weight determination by the Rast method. Physical and analytical data are given in Table 1. Structure determination studies used the following spectral data: IR (Table 2), ^{1}H NMR (Table 3) and Mössbauer (Table 4).

Infrared spectra

These spectra were recorded in KBr in the 4000–200 cm^{-1} range and the important frequencies of interest are $\nu_{asym}(COO)$, $\nu_{sym}(COO)$, $\nu(N \rightarrow O)$, $\nu(Sn-C)$ and $\nu(Sn-O)$. Complex formation is confirmed by the disappearance of a broad band present in the 2600–2200 cm^{-1} range in the case of isonicotinic acid (2600–2400 cm^{-1}, isonicotinic acid N-oxide). These two acids can coordinate to tin(IV) in a unidentate, bidentate or bridging bidentate manner. These modes of coordination may be distinguished by the $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ values of the carboxylate group and the magnitude of their arithmetic difference, the $\Delta\nu$ value, $\Delta\nu = \nu_{asym}(COO) - \nu_{sym}(COO)$. $\Delta\nu$ in the case of 1:1 and 2:1 complexes of isonicotinic acid (220 ± 25 cm^{-1}) are lower than that observed in the case of the free acid (375 cm^{-1}) and are comparable to that observed in the case of sodium isonicotinate (210 cm^{-1}). Hence the carboxylate group is bonded to tin(IV) in a bidentate manner [4]. However, in some of these complexes two values of $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ each take two values which demonstrates the presence of two different patterns of bonding of the carboxylate groups distorting the geometry.

In the case of the 2:1 dimethyl- and dibenzyltin derivatives **9** and **12** the $\Delta\nu$ value is 300 cm^{-1} which is lower than that of the isonicotinic acid N-oxide but is higher than that of its sodium salt showing thereby unidentately bonded carboxylates. However, the dibutyl- and dioctyltin complexes contain a free C=O and a coordinated C=O group as indicated by $\Delta\nu$ values 365 and 240 ± cm^{-1}. Two values of $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ are observed in the case of 1:1 monomeric dinuclear dibutyl and the dioctyl complexes **14** and **15** with $\Delta\nu$ values comparable to the sodium salt of isonicotinic acid N-oxide. In the case of the polymeric dinuclear dimethyl and dibenzyl complexes 13 and 16 only one $\nu_{asym}(COO)$ and one $\nu_{sym}(COO)$ value are observed. In each case the $\Delta\nu$ value is higher than that in the sodium isonicotinate N-oxide showing thereby the unidentate nature of the two carboxylate groups [6].

The $\nu(N \rightarrow O)$ values in ^{i}NicOH and ^{i}NicONa are 1205 and 1230 cm^{-1} whereas in the 2:1 dimethyl and dibenzyl complexes **9** and **12**, it appears at 1200 and 1205 cm^{-1}. As compared to the ^{i}NicONa, there is a clear decrease by 30 cm^{-1} which suggests coordination from oxygen of N-oxide to tin(IV) [1]. In the case of the dibutyl and dioctyl complexes, **10** and **11**, two strong bands at 1230 and 1210 cm^{-1} indicate one free N-oxide group and one coordinated to tin(IV). In the 1:1 dinuclear complexes dimethyl and dibenzyl **13** and **16**, both the N-oxide oxygens are coordinated to tin(IV) as shown by a decrease in the $\nu(N \rightarrow O)$ value of 30

Table 1

Analytical and physical data of the complexes of ^{i}NicH and ^{i}NicOH

No.	Complex	Colour	Yield (%)	M.p. (°C)	Analysis found (calc.) (%)				Mol.wt. found (calc.)	n^*
					C	H	N	Sn		
1	$(CH_3)_2Sn(^{i}Nic)_2$ [a]	Dirty white	58	257–258	42.85 (42.86)	4.26 (3.57)	7.37 (7.14)	29.75 (30.23)	*I*	P
2	$(^{n}C_4H_9)_2Sn(^{i}Nic)_2$ [b]	Off-white	60	*I*	50.34 (50.42)	5.54 (5.46)	5.63 (5.88)	24.83 (24.90)	500 (476.7)	M
3	$(^{n}C_8H_{17})_2Sn(^{i}Nic)_2$ [b]	Yellowish white	55	*I*	56.95 (57.14)	7.12 (7.14)	4.35 (4.76)	20.38 (20.16)	560 (588.7)	M
4	$(C_6H_5CH_2)_2Sn(^{i}Nic)_2$ [a]	Off-white	61	221–223	–	3.87 (4.04)	5.45 (5.15)	22.14 (22.79)	*I*	P
5	$[(CH_3)_2Sn(^{i}Nic)]_2O$ [a]	Light-brown	52	Above 300	34.27 (34.53)	4.13 (3.60)	5.19 (5.04)	42.31 (42.59)	*I*	P
6	$[(^{n}C_4H_9)_2Sn(^{i}Nic)]_2O$ [b]	Off-white	65	137–139	45.87 (46.41)	6.16 (6.08)	3.84 (3.73)	32.11 (32.76)	703 (725.4)	M
7	$[(^{n}C_8H_{17})_2Sn(^{i}Nic)]_2O$ [b]	Yellowish white	49	101–102	55.36 (55.70)	7.85 (8.02)	3.10 (2.95)	24.88 (25.01)	937.7 (949.4)	M

8	$[(C_6H_5CH_2)_2Sn(^iNic)]_2O$ [a]	Off-white	64	232–234	–	3.98	3.36	26.66	*I*	P
						(4.19)	(3.26)	(27.16)		
9	$(CH_3)_2Sn(^iNicO)_2$ [a]	White	61	264–266	39.75	3.14	7.02	27.70	*I*	P
					(39.62)	(3.30)	(6.60)	(27.99)		
10	$(^nC_4H_9)_2Sn(^iNicO)_2$ [d]	Purple	55	131–132	46.56	4.85	5.37	23.63	471	M
					(47.24)	(5.12)	(5.51)	(23.37)	(508.7)	
11	$(^nC_8H_{17})_2Sn(^iNicO)_2$ [d]	Light brown	56	148–150	53.85	7.87	4.65	18.90	572	M
					(54.19)	(6.77)	(4.52)	(19.15)	(620.7)	
12	$(C_6H_5CH_2)_2Sn(^iNicO)_2$ [c]	Brown	62	190–192	53.93	3.70	4.94	20.65	*I*	P
					(54.17)	(3.82)	(4.86)	(20.61)		
13	$[(CH_3)_2Sn(^iNicO)]_2O$ [c]	Off-white	59	Above 300	32.24	3.50	5.23	39.78	*I*	P
					(32.65)	(3.40)	(4.76)	(40.37)		
14	$[(^nC_4H_9)_2Sn(^iNicO)_2O$ [d]	Yellowish brown	53	128–129	44.94	5.63	3.99	30.98	724	M
					(44.44)	(5.82)	(3.70)	(31.40)	(757.4)	
15	$[(^nC_8H_{17})_2Sn(^iNicO)]_2O$ [d]	Yellowish brown	55	*l*	53.96	7.32	3.16	24.43	976	M
					(53.80)	(7.76)	(2.86)	(24.22)	(981.4)	
16	$[(C_6H_5CH_2)_2Sn(^iNicO)]_2O$ [c]	Pale yellow	57	181–184	53.41	3.73	3.82	27.01	*I*	P
					(53.81)	(4.04)	(3.14)	(27.80)		

^{i}NicH = isonicotinic acid; ^{i}NicOH = isonicotinic acid N-oxide; M-Monomer; P = Polymer; n^* = molecular complexity; *I* = Insoluble in camphor; *l* = viscous liquid. [a] Crystallized from dry methanol or ethanol. [b] Washed with hot dry methanol or ethanol. [c] Washed with dry benzene + dry methanol mixture (1:1) or benzene + ethanol or methanol + ethanol mixture (1:1). [d] Crystallized from dry benzene and methanol.

Table 2

IR data of ^{i}NicH and ^{i}NicOH complexes (cm^{-1})

	Complex	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	$\nu(N \rightarrow O)$	$\nu(Sn-C)$	$\nu(Sn-O)$	$\nu(Sn-O-Sn)$
	^{i}NicH	1710s	1335s	375	–	–	–	–
	Na^{i}Nic	1610s	1400s	210	–	–	–	–
1	$(CH_3)_2Sn(^{i}Nic)_2$	1590s	1350s	240	–	585m	425s	–
						495m		
2	$(^{n}C_4H_9)_2Sn(^{i}Nic)_2$	1638m	1410s	226	–	600sh	420s	–
		1595s	1400s	195		495m		
3	$(^{n}C_8H_{17})_2Sn(^{i}Nic)_2$	1595s	1400s	195	–	610m	480s	–
		1645s	1345s	245		555w	455w	
							415s	
4	$(C_6H_5CH_2)_2Sn(^{i}Nic)_2$	1600s	1335m	265	–	430m	490s	–
5	$[(CH_3)_2Sn(^{i}Nic)]_2O$	1635s	1405s	230	–	580w	495s	645s
		1595s	1345s	250		525sh	427s	
6	$[(^{n}C_4H_9)_2Sn(^{i}Nic)]_2O$	1635s	1405s	230	–	605s	495s	675s
		1595s	1340s	255		520sh	415s	
7	$[(^{n}C_8H_{17})_2Sn(^{i}Nic)]_2O$	1635s	1400s	235	–	610s	492m	670s
		1590s	1345s	245		555m	420s	

8	$[(C_6H_5CH_2)_2Sn(^iNic)]_2O$	1590sh	1340sh	250	–	420m	485m	640s
		1600s	1400s	200			427s	
	^{i}NicOH	1700s	1300s	400	1205sh	–	–	–
	Na^{i}NicO	1600s	1370bs	230	1230s	–	–	–
9	$(CH_3)_2Sn(^iNicO)_2$	1649s	1349s	300	1200s	579m	455s	–
						551m	400w	
10	$(^nC_4H_9)_2Sn(^iNicO)_2$	1705s	1340s	365	1230s	600sh	465m	–
		1620s	1390s	230	1210sh	538s	385m	–
11	$(^nC_8H_{17})_2Sn(^iNicO)_2$	1700s	1335s	365	1230s	625s	460m	–
		1640s	1390s	250	1215s	535s	338m	
12	$(C_6H_5CH_2)_2Sn(^iNicO)_2$	1642s	1340s	302	1205s	450m	385w	–
							360m	
13	$[(CH_3)_2Sn(^iNicO)]_2O$	1640s	1349s	291	1200s	575m	450s	645s
						551m	435s	
14	$[(^nC_4H_9)_2Sn(^iNicO)]_2O$	1650sh	1390s	260	1230s	600sh	470m	640s
		1600s	1355sh	245	1190m	580m	395mb	
15	$[(^nC_8H_{17})_2Sn(^iNicO)]_2O$	1705s	1350s	355	1239s	575m	475s	640
		1600s	1380s	220	1195m	540m		
16	$[(C_6H_5CH_2)_2Sn(^iNicO)]_2O$	1642s	1335s	307	1203s	480sh	451m	635s
							360m	

s = strong, bs = broad strong, bw = broad weak, w = weak, sh = shoulder, m = medium, ^{i}NicH = isonicotinic acid; Na^{i}Nic = sodium salt of isonicotinic acid; ^{i}NicOH = isonicotinic acid N-oxide; Na^{i}NicO = sodium salt of isonicotinic acid N-oxide.

Table 3

^{1}H NMR of ^{i}Nic [a] and ^{i}NicO complexes [b] (scale-δ ppm)

No	Complex	Aliphatic protons			Aromatic protons	
		CH_3	CH_2	CH_2Sn	H^3 H^5	H^2 H^6
	^{i}NicH [a]	–	–	–	8.75 (m, 2H)	9.00 (m, 2H)
	^{i}NicOH [a]	–	–	–	8.42–8.76 (m, 2H)	8.77–9.32 (m, 2H)
2	$(^nC_4H_9)_2Sn(^iNic)_2$	0.875 (m, 6H)	1.12–1.85 (m, 12H)		7.85 (m, 4H)	8.75 (m, 4H)
3	$(^nC_8H_{17})_2Sn(^iNic)_2$	0.825 (m, 6H)	1.20 (m, 24H)	1.62 (m, 4H)	7.80 (m, 4H)	8.72 (m, 4H)
6	$[(^nC_4H_9)_2Sn(^iNic)]_2O$	0.875 (m, 12H)	1.12–1.85 (m, 24H)		7.77 (m, 4H)	8.75 (m, 4H)
7	$[(^nC_8H_{17})_2Sn(^iNic)]_2O$	0.850 (m, 12H)	1.22 (m, 48H)	1.62 (m, 8H)	7.80 (m, 4H)	8.75 (m, 4H)
10	$(^nC_4H_9)_2Sn(^iNicO)_2$	0.875 (t, 6H)	1.05–1.85 (m, 12H)		7.92 (m, 4H)	8.27 (m, 4H)
11	$(^nC_8H_{17})_2Sn(^iNicO)_2$	0.825 (m, 6H)	1.25 (m, 24H)	1.62 (m, 4H)	7.80 (m, 4H)	8.17 (m, 4H)
14	$[(^nC_4H_9)_2Sn(^iNicO)]_2O$	0.90 (m, 12H)	1.07–1.82 (m, 24H)		7.87 (m, 4H)	8.25 (m, 4H)
15	$[(^nC_8H_{17})_2Sn(^iNicO)]_2O$	0.825 (m, 12H)	1.25 (m, 48H)	1.57 (m, 8H)	7.75 (m, 4H)	8.125 (m, 4H)

t = triplet, m-multiplet, [a] trifluoroacetic acid, [b] $CDCl_3$. ^{i}NiCH = isonicotinic acid, ^{i}NicOH = isonicotinic acid N-oxide.

cm^{-1}. In the case of 1:1 dibutyl and dioctyl complexes **14** and **15** one N-oxide oxygen remains free as the $\nu(N \rightarrow O)$ value remains unshifted and one is coordinated to tin.

The ν(Sn–O) has been observed as weak to strong bands in the 400–500 cm^{-1} region in all the 1:1 and 2:1 isonicotinate complexes and in the case of isonicotinic acid N-oxide complexes in the 400–500 cm^{-1} and 300–400 cm^{-1} region. The identification of ν(Sn–O) in the specified range confirms coordination to tin(IV) from the carboxylate oxygen in the case of isonicotinic acid but in the case of isonicotinic acid N-oxide the two ranges of ν(Sn–O) indicate that one of the oxygens of the carboxylate group coordinates to tin(IV) and the coordination of the other oxygen to tin(IV) arises from the N-oxide oxygen from the other molecule. In the 1:1 complexes of isonicotinic acid a strong band in the range 640–675 cm^{-1} is assigned to ν(Sn–O–Sn) but the same is assigned at 640 ± 5 cm^{-1} in the case of 1:1 complexes of isonicotinic acid N-oxide [5]. The appearance of two ν(Sn–C) values in the complexes shows a non-linear or *cis* position of the R groups.

^{1}H NMR spectra

The spectra of the soluble complexes (dibutyl and dioctyl) have been recorded in $CDCl_3$ and of acids in trifluoroacetic acid (Table 3, δ-scale). The total number of protons counted from the integration curve tallies with the total number of protons calculated from the expected molecular formula.

Table 4

Mössbauer data at 80 K (mm s^{-1})

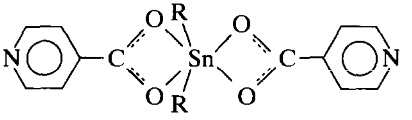
No	Complex	IS	QS	Line	Widths	Coordination
9	$(CH_3)_2Sn(^iNicO)_2$	1.36	4.00	1.15	1.16	*Trans* 6 coord.
10	$(^nC_4H_9)_2Sn(^iNicO)_2$	1.35	3.78	0.80	0.85	*Trans* 6 coord.
11	$(^nC_8H_{17})_2Sn(^iNicO)_2$	1.30	3.30	0.83	1.10	*Trans* 6 coord.
13	$[(CH_3)_2Sn(^iNicO)]_2O$	1.29	4.17	0.79	0.92	*Trans* 6 coord.
		0.94	2.16	1.02	0.75	*Trans* 5 coord.
14	$[(^nC_4H_9)_2Sn(^iNicO)]_2O$	1.12	3.32	0.80	0.91	*Trans* 5 coord.
		1.49	3.49	0.78	0.85	*Trans* 5 coord.

IS = Isomer shift, QS = Quadrupole splitting.

In the case of the two acids (see **e**, **f** above) the H^2 and H^6 protons appear as a multiplet at a lower field as compared to the higher field multiplet due to H^3 and H^5. On formation of the complex both the multiplet signals shift upfield and the upfield shift is higher in the H^4 and H^5 protons. This may be due to their position nearer to the coordinating group.

Mössbauer spectra

Mössbauer parameters of some complexes are reported in Table 4. The isomer shift (IS) and quadrupole splitting (QS) values for complex **9** fall in the range of a regular trans octahedral structure whereas for complexes **10** and **11** the values do suggest a five coordinate structure but a distorted octahedral structure cannot be ruled out. Distortion from a regular octahedron can give values as those observed for five coordinate complexes [7,8]. The 1:1 dinuclear isonicotinic acid N-oxide complexes **13** and **14** show two types of IS and QS values which further indicate five and six coordinate environments respectively for the two tin(IV) atoms which coexist in the molecule [1,2].



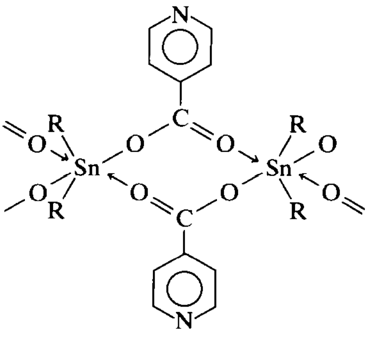


Fig. 1. Distorted octahedral structure proposed for 2:1 complexes with isonicotinic acid.

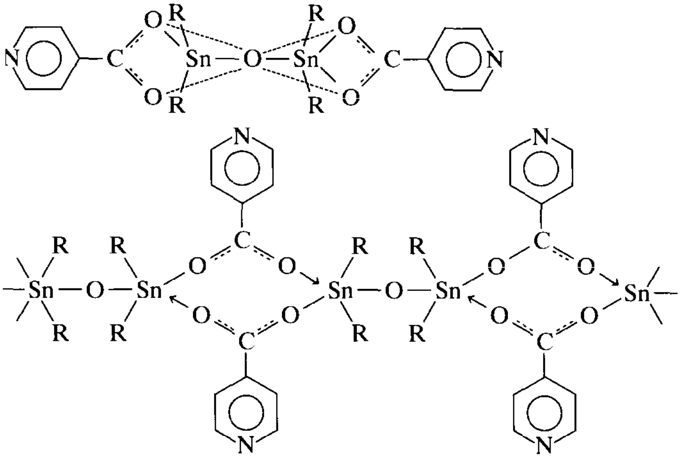
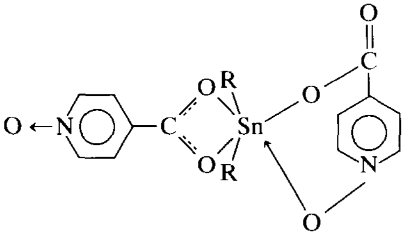
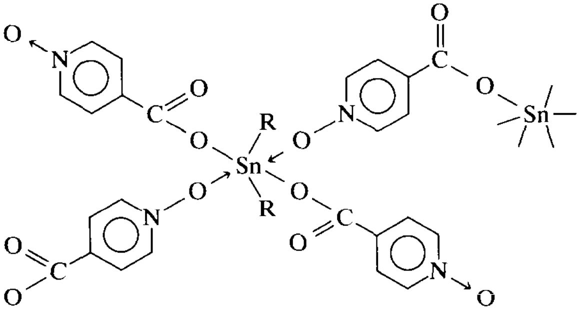


Fig. 2. Five-coordinate trigonal bipyramid structure proposed for 1 : 1 complexes with isonicotinic acid.



($R = n\text{-}C_4H_9, n\text{-}C_8H_{17}$)



($R = CH_3, C_6H_5CH_2$)

Fig. 3. Structure proposed for 2 : 1 complexes with isonicotinic acid N-oxide.

Conclusion

The spectral data confirm a distorted octahedral structure (Fig. 1) for all 2 : 1 and a five coordinate trigonal bipyramid structure (Fig. 2) for the 1 : 1 complexes with isonicotinic acid. Infrared and Mössbauer spectra data support the structures presented in Fig. 3 for the 2 : 1, and in Fig. 4 for the 1 : 1 complexes with isonicotinic acid N-oxide.

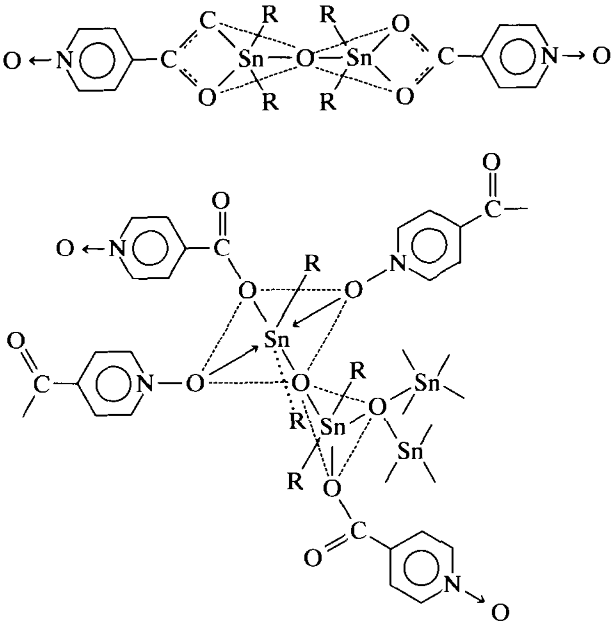


Fig. 4. Structure proposed for 1:1 complexes with isonicotinic acid N-oxide.

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