Journal of Organometallic Chemistry, 411 (1991) 89–98
Elsevier Sequoia S.A., Lausanne
JOM 21707

Preparation and tin-119*m* Mössbauer spectra of diorganotin(IV) complexes of picolinic acid and picolinic acid *N*-oxide

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(Received January 8th, 1991)

Abstract

Two types of complexes of diorganotin picolinates (i) $R_2Sn(Pic)_2$ [2:1] and (ii) $[R_2SnPic]_2O$ [1:1] and of diorganotinpicolinate *N*-oxides (i) $R_2Sn(PicO)_2$ [2:1] and (ii) $[R_2SnPicO]_2O$ [1:1] ($R = CH_3$, n-C_4H_9, n-C_8H_{17}, $C_6H_5CH_2$) have been prepared by reacting picolinic acid and picolinic acid *N*-oxide with diorganotin oxide in 2:1 and 1:1 ligand:metal molar ratio. The methyl and benzyl derivatives are less soluble in organic solvents whereas the butyl and octyl derivatives are more soluble. A unidentate carboxylate is present in all the complexes. However, a weak interaction such as $C{=}O \rightarrow Sn$ cannot be ruled out in the less soluble complexes. In the picolinates the ring nitrogen coordinates to tin(IV) intramolecularly in the butyl and octyl derivatives and intra- and intermolecularly in the methyl and benzyl derivatives. Mössbauer parameters show a distorted *trans* octahedral structure for the 2:1 derivatives and a distorted *trans* trigonal bipyramidal structure for the 1:1 picolinates with an Sn–O–Sn bridge. A mixed distorted *trans* octahedral tin atom geometry and a distorted *trans* trigonal bipyramidal tin with an Sn–O–Sn bridge are found in the same molecule in the 1:1 complexes of picolinic acid *N*-oxide.

Introduction

Only few triorganotin [1,2] and diorganotin [3,4] complexes with pyridine carboxylic acid are known. A crystal and molecular structure determination of $Me_2(Cl)SnPic$-2 has revealed the presence of an Sn–N bond and a distorted *trans* octahedral geometry around the tin atom [5]. Present interest in the diorganotin complexes of picolinic acid and picolinic acid *N*-oxide is focused on the nature of bonding and structures.

Experimental

Diorganotin oxides were procured from Alfa Inorganics; picolinic acid and picolinic acid *N*-oxide were purchased from Aldrich and used as such.

Physical measurements

Elemental analyses were carried out by the Micro-analytical Service, Calcutta University, Calcutta. Tin was estimated as SnO_2. Molecular weights were determined in camphor (175 ° C) by the Rast method. No cryoscopic molecular weight determination could be carried out because of the less soluble nature of the complexes at low temperature. Infrared spectra were recorded on Spectromom 1000 (4000–700 cm^{-1}) and Pye Unicam SP 3-300 (4000–200 cm^{-1}) spectrophotometers. ^1H NMR spectra were recorded in $CDCl_3$ and trifluoroacetic acid on a Tesla BS-487C, 80 MHz instrument. Mössbauer spectra were recorded with a Harwell 6000 series spectrometer with samples cooled by liquid nitrogen (80 K) and the source (Pd–Sn) at room temperature. Isomer shifts are relative to SnO_2 measured at room temperature.

Preparation of complexes

The 1 : 1 and 2 : 1 complexes were prepared by dissolving the ligand (0.001 mol for 1 : 1 and 0.002 mol for 2 : 1 derivatives in dry benzene (50 cm^3) and adding diorganotin oxide (0.001 mol) to each solution. The solutions were refluxed for 4–5 h on a water bath using a Dean Stark trap. In case of all butyl and octyl derivatives clear solutions resulted whereas white solids were obtained for all methyl and benzyl derivatives. Solvent was removed from the soluble complexes by distillation under reduced pressure leaving solids behind, whereas the insoluble complexes were separated by filtration. The butyl and octyl complexes were recrystallised from dry methanol and the methyl and benzyl complexes were crystallized or washed with a 1 : 1 mixture of dry methanol and dry ethanol.

Results and discussion

The 2 : 1 and the 1 : 1 diorganotin(IV) complexes of picolinic acid and picolinic acid *N*-oxide listed in Table 1 were prepared as described in the Experimental section. These compounds were identified by elemental analysis (Table 1), infrared (Table 2), ^1H NMR (Table 3) and Mössbauer spectroscopy (Table 4). The butyl and octyl derivatives are more soluble than the methyl and benzyl derivatives. Molecular weight measurements by the Rast method show the butyl complexes and octyl compounds to exist as monomers and the methyl and benzyl complexes as polymers. However, a weak polymeric nature of the monomers at room temperature is not ruled out. Structural proposals are based on the infrared and Mössbauer data.

Infrared spectra

The absorption bands important for structure assignment are given in Table 2. The type of coordination of the carboxylate group is decided on the basis of the magnitude of separation ($\Delta\nu$) of the $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ bands and is compared with that of sodium salt of the acids. For each complex two $\nu(COO)_{asym}$ values around 1670 and 1650 cm^{-1} and two $\nu(COO)_{sym}$ values around 1380 and 1340 cm^{-1} have been observed. The $\Delta\nu$ values in all complexes were found to be much higher than those in the corresponding sodium salts of the acids. This comparison clearly shows that the carboxylate group is unidentate [6,7]. However, a weak O–C=O → Sn interaction in the solid state cannot be ruled out. An asymmetric position of the two carboxylate groups in all 1 : 1 and 2 : 1 complexes is

Table 1. Analytical and physical data of the complexes of PicH and PicOH [a]

	Complex	Colour	Yield (%)	M.P. (°C)	Analysis (%) Found (Calc.) Mol. wt.					n [d]
					C	H	N	Sn	Found (Calc.)	
1	$(CH_3)_2Sn(Pic)_2$ [b]	white	56	255–257	42.76 (42.65)	4.43 (3.45)	7.05 (7.32)	30.24 (30.24)	I	P
2	$(n\text{-}C_4H_9)_2Sn(Pic)_2$ [c]	off white	63	193–194	50.11 (50.24)	5.06 (5.23)	6.37 (5.62)	24.46 (24.94)	529 (476)	M
3	$(n\text{-}C_8H_{17})_2Sn(Pic)_2$ [c]	white	54	144–145	57.40 (57.20)	7.07 (7.02)	5.07 (4.64)	20.47 (20.19)	617 (588)	M
4	$(C_6H_5CH_2)_2Sn(Pic)_2$ [b]	flesh	53	176–177	57.40 (57.35)	4.37 (4.04)	4.76 (5.15)	21.50 (21.79)	I	P
5	$[(CH_3)_2Sn(Pic)]_2O$ [b]	white	57	280–281	33.97 (34.53)	3.53 (3.63)	5.55 (5.04)	42.85 (42.59)	I	P
6	$[(n\text{-}C_4H_9)_2Sn(Pic)]_2O$ [c]	white	60	203–204	46.60 (46.41)	6.74 (6.39)	4.19 (3.62)	33.20 (32.79)	717 (724)	M
7	$[(n\text{-}C_8H_{17})_2Sn(Pic)]_2O$ [c]	white	56	105–107	55.55 (55.65)	8.08 (8.21)	3.32 (2.74)	25.33 (25.04)	876 (948)	M
8	$[(C_6H_5CH_2)_2Sn(Pic)]_2O$ [b]	off white	61	162–163	56.41 (55.81)	4.41 (4.19)	2.86 (3.26)	27.21 (27.56)	I	P
9	$(CH_3)_2Sn(PicO)_2$ [b]	dirty white	71	193–194	39.30 (38.52)	4.05 (3.85)	6.93 (6.62)	27.50 (27.95)	I	P
10	$(n\text{-}C_4H_9)_2Sn(PicO)_2$ [c]	brownish yellow	69	165–166	47.82 (47.63)	5.42 (5.02)	5.48 (5.50)	23.36 (23.67)	500 (508)	M
11	$(n\text{-}C_8H_{17})_2Sn(PicO)_2$ [c]	light brown	79	120–122	54.58 (54.25)	7.63 (6.77)	4.57 (4.56)	20.33 (19.65)	615 (620)	M
12	$(C_6H_5CH_2)_2Sn(PicO)_2$ [b]	yellowish brown	77	126–128	54.11 (54.10)	3.89 (3.82)	5.35 (4.86)	20.37 (20.61)	I	P
13	$[(CH_3)_2Sn(PicO)]_2O$ [b]	dirty white	67	> 300	32.38 (32.65)	3.45 (3.40)	5.22 (4.76)	40.80 (40.28)	I	P
14	$[(n\text{-}C_4H_9)_2Sn(PicO)]_2O$ [b]	brownish yellow	79	178–179	44.53 (44.64)	6.71 (5.91)	4.01 (3.75)	31.63 (31.40)	747 (756)	M
15	$[(n\text{-}C_8H_{17})_2Sn(PicO)]_2O$ [c]	light brown	72	140–142	53.26 (53.87)	7.80 (7.76)	3.08 (2.85)	24.15 (24.22)	999 (980)	M
16	$[(C_6H_5CH_2)_2Sn(PicO)]_2O$ [b]	yellowish brown	55	169–171	52.96 (53.73)	3.82 (4.17)	2.85 (3.13)	28.08 (27.80)	I	P

[a] PicH = picolinic acid, PicOH = picolinic acid *N*-oxide. [b] Crystallized from methanol/ethanol mixture (1:1). [c] Crystallized from dry methanol. [d] n = degree of complexity. M = monomer. P = polymer. I = insoluble in camphor.

Table 2

IR data for picolinic acid and picolinic acid *N*-oxide complexes (cm^{-1})

	Complex	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$	$\nu(N-O)$	$\nu(Sn-C)$	$\nu(Sn-O)$	$\nu(Sn-O-Sn)$	$\nu(Sn-N)$
	PicH	1710s	1300s	400	–	–	–	–	–
	Na-Pic	1645s	1410w	235	–	–	–	–	–
1	$(CH_3)_2Sn(Pic)_2$	1675s	1385s	290	–	585m	430m	–	372w
		1625s	1350s	275		545m	325m		355w
2	$(n\text{-}C_4H_9)_2Sn(Pic)_2$	1670s	1385s	285	–	600w	425s	–	395w
		1630s	1350s	280		540m			
3	$(n\text{-}C_8H_{17})_2Sn(Pic)_2$	1670s	1385s	285	–	605w	425s	–	350w
		1625s	1345s	280		540m			
4	$(C_6H_5CH_2)_2Sn(Pic)_2$	1675s	1380s	295	–	535m	430s	–	390w
		1625s	1345s	280		452m	410m		370w
5	$[(CH_3)_2Sn(Pic)]_2O$	1680s	1385s	295	–	550m	430s	635m	370w
		1630s	1350s	280		520m			360w
6	$[(n\text{-}C_4H_9)_2Sn(Pic)]_2O$	1670s	1375s	295	–	600s	425m	680m	390w
		1645s	1345s	300		525s			375w
7	$[(n\text{-}C_8H_{17})_2Sn(Pic)]_2O$	1670s	1380sh	290	–	605s	425m	675m	380w
		1650s	1340s	310		570s	415m		340w
8	$[(C_6H_5CH_2)_2Sn(Pic)]_2O$	1675s	1370s	305	–	560m	445m	635m	390w
		1650s	1360s	290		510s	420sh		375w
	PicOH	1720s	1370w	350	1230sh	–	–	–	–
	Na-PicO	1625s	1370s	255	1230s	–	–	–	–

9	$(CH_3)_2Sn(PicO)_2$	1678s	1368sh	310	1223m	582s	481m	–	–
		1650s	1345s	306	1202s	522w			
10	$(n\text{-}C_4H_9)_2Sn(PicO)_2$	1720sh	1340s	380	1210s	595m	480m	–	–
		1655svb		315		575s	440w		
						550s			
11	$(n\text{-}C_8H_{17})_2Sn(PicO)_2$	1710sh	1345s	385	1220m	595s	440m	–	–
		1650s	1335s	315		575s			
12	$(C_6H_5CH_2)_2Sn(PicO)_2$	1720sh	1345s	325	1220m	565s	492m	–	–
		1670s	1330s	340	1197s	555s	450m		
							405m		
13	$[(CH_3)_2Sn(PicO)]_2O$	1665sh	1350s	315	1210s	575s	490m	675s	–
		1645s		290	1230m	512m	440bw		
							402m		
14	$[(n\text{-}C_4H_9)_2Sn(PicO)]_2O$	1660sb	1345	305	1210s	604sh	480m	675s	–
		1640sh	1380	280		580s	480m		
						550s	400m		
15	$[(n\text{-}C_8H_{17})_2Sn(PicO)]_2O$	1660sh	1382sh	305	1208m	600sh	550s	672s	–
		1645sb	1340s	278	1198s	575s	480m		
						585s	400m		
16	$[(C_6H_5CH_2)_2Sn(PicO)]_2O$	1670sh	1345s	335	1198s	585s	490m	675s	–
		1660s	1330s	330	1205m	550s	450m		
						450m	402m		

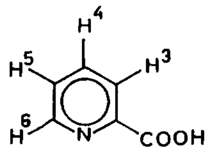
PicH = picolinic acid. Na-Pic = sodium salt of picolinic acid, PicOH = picolinic acid *N*-oxide, Na-Pico = sodium salt of picolinic acid *N*-oxide. w = weak, s = strong, v = very, b = broad, sh = shoulder, m = medium.

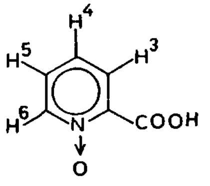
evidenced by the presence of two ν(COO) values, showing that the complexes have distorted structures.

In the case of butyl and octyl complexes of picolinic acid *N*-oxide one strong to medium band is observed around 1210 cm^{-1} whereas in the methyl and benzyl derivatives two bands are observed around 1210 and 1198 cm^{-1}. In comparison with the ν(N–O) band present at 1230 cm^{-1} in the sodium salt of picolinic acid *N*-oxide, these bands are lowered by about 10–20 cm^{-1}. This decrease in ν(N–O) shows that the *N*-oxide oxygen is coordinated to tin(IV) [8]. The presence of two bands in the methyl and benzyl derivatives indicates two types of *N*-oxide oxygen bonding, which may be intra- and intermolecular bonding. The two ν(Sn–C) values show that the alkyl/aryl groups are at non-linear positions. The ν(Sn–O) band has also been observed in the specified range [6,7]. In case of all the picolinic acid complexes a new band in the range 390–350 cm^{-1} is noted and assigned to an Sn → N bond [5,9]. The presence of two ν(Sn–N) bands in some complexes shows that the two Sn–N bonds are nonequivalent, which may also correspond to intra- and intermolecular coordination from nitrogen to tin. This band is absent in the case of picolinic acid *N*-oxide complexes. In the case of 1:1 picolinic acid complexes a new band present in the range 680–635 cm^{-1} is assigned to an Sn–O–Sn bridge whereas in the 1:1 picolinic acid *N*-oxide complexes a strong band in 675–672 cm^{-1} range is assigned to Sn–O–Sn [10].

^{1}H NMR spectra

The ^{1}H NMR spectra of picolinic acid and picolinic acid *N*-oxide were recorded in trifluoroacetic acid and those of the soluble complexes in CDCl$_3$. The results are listed in Table 3. In the case of dibutyl- and dioctyl-tin (IV) complexes the signals for all types of protons have been identified and the number of protons of various groups observed from the integration curve are found to be equivalent to the total number of protons calculated from the expected molecular formula.





In the case of ring protons the H^4 signal is shifted upfield in all the soluble complexes whereas the H^6 signal is moved slightly downfield in the 2:1 complexes of picolinic acid and slightly upfield in the 1:1 complexes. In all the picolinic acid *N*-oxide complexes the H^6 signal is shifted upfield. The H^3 and H^5 proton signals also undergo a minor change. The maximum effect of upfield or downfield shift is undergone by the H^4 and H^6 proton signals, which is probably due to their position near the coordinating groups. The nature of the spectra of all the complexes is complex. The presence of multiplet signals for alkyl or aryl groups indicates the non-equivalence of R groups in non-linear *trans* positions.

Mössbauer data

The tin-119*m* Mössbauer data have been recorded at liquid nitrogen temperature (80 K) and are given in Table 4. The Mössbauer parameters of 2:1 complexes are in

Table 3

^1H NMR data for picolinic acid and picolinic acid *N*-oxide complexes [a] (δ, ppm)

	Complexes	Aliphatic protons			Aromatic protons			
		$-CH_3$	$-CH_2$	$-CH_2Sn$	H^4	H^5	H^6	H^3
	PicH [b]	–	–	–	8.77 (m,2H)		8.37 (m,1H)	8.97 (m,1H)
	PicOH [b]	–	–	–	8.70 (d,2H)		7.87–8.50 (m,2H)	
2	$(n-C_4H_9)_2Sn(Pic)_2$	0.75 (t,6H)	1.05–2.17 (m,12H)		7.62 (m,2H)	7.80 (m,2H)	8.45 (m,2H)	8.85 (m,2H)
3	$(n-C_8H_{17})_2Sn(Pic)_2$	0.825 (m,6H)	1.14 (m,24H)	1.35 (m,4H)	7.65 (m,2H)	8.05 (m,2H)	8.42 (m,4H)	8.90 (m,2H)
6	$[(n-C_4H_9)_2Sn(Pic)]_2O$	0.75 (m,12H)	0.92–1.80 (m,24H)		7.50 (m,2H)	7.87 (m,2H)	8.25 (m,4H)	8.88 (m,2H)
7	$[(n-C_8H_{17})_2Sn(Pic)]_2O$	0.80 (m,12H)	1.17 (m,48H)	1.70 (m,8H)	7.50 (m,2H)	7.85 (m,2H)	8.25 (m,2H)	8.85 (m,2H)
10	$(n-C_4H_9)_2Sn(PicO)_2$	0.80 (m,6H)	0.97–1.80 (m,12H)		7.57 (m,4H)		8.17 (m,4H)	
11	$(n-C_8H_{17})_2Sn(PicO)_2$	0.85 (m,6H)	1.00–1.87 (m,28H)		7.62 (m,4H)		8.30 (m,4H)	
12	$[(n-C_4H_9)_2Sn(PicO)]_2O$	0.85 (m,12H)	1.00–1.82 (m,24H)		7.40 (m,4H)	7.95 (m,2H)		8.25 (m,2H)
13	$[(n-C_8H_{17})_2Sn(PicO)]_2O$	0.82 (m,12H)	1.22 (m,48H)	1.47 (m,8H)	7.75 (m,4H)		8.25 (m,4H)	

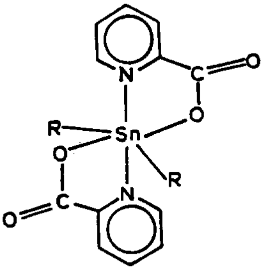
[a] All complexes soluble in $CDCl_3$. PicH = picolinic acid. PicOH = picolinic acid *N*-oxide. [b] Trifluoroacetic acid.

Table 4

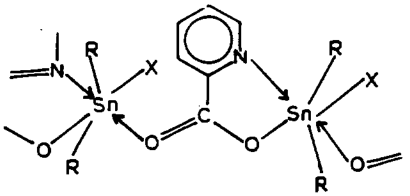
Mössbauer data at 80 K (mm s^{-1})

No.	Complex	IS	QS	Γ_1	Γ_2	Expected coordination
3	$(n\text{-}C_8H_{17})_2Sn(Pic)_2$	1.45	4.26	0.75	0.80	*trans* 6
6	$[(n\text{-}C_4H_9)_2Sn(Pic)]_2O$	1.30	3.33	0.92	1.20	*trans* 5
9	$(CH_3)_2Sn(PicO)_2$	1.27	3.61	1.03	–	*trans* 6
10	$(n\text{-}C_4H_9)_2Sn(PicO)_2$	1.38	3.81	0.95	–	*trans* 6
11	$(n\text{-}C_8H_{17})_2Sn(PicO)_2$	1.52	3.74	1.06	0.74	*trans* 6
13	$[(CH_3)_2Sn(PicO)]_2O$	1.24	3.89	0.93	–	*trans* 6
		1.00	2.50	1.12		*trans* 5
14	$[(n\text{-}C_4H_9)_2Sn(PicO)]_2O$	1.29	3.92	1.00	–	*trans* 6
		1.17	2.95	0.99		*trans* 5
15	$[(n\text{-}C_8H_{17})_2Sn(PicO)]_2O$	1.53	3.76	1.06	0.64	*trans* 6
		1.20	3.10	1.00	0.84	*trans* 5

the range IS = 1.27–1.52, QS = 3.61–4.26, showing a coordination number higher than four for tin. It has been observed that a distortion from a a regular octahedral conformation can give values similar to those observed for five-coordinate compounds [11]; the quadrupole splitting (QS) value is known to be mainly governed by the C–Sn–C bond angle when the donor atoms are highly electronegative [12,13].

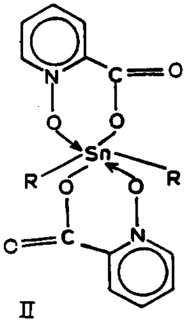


I



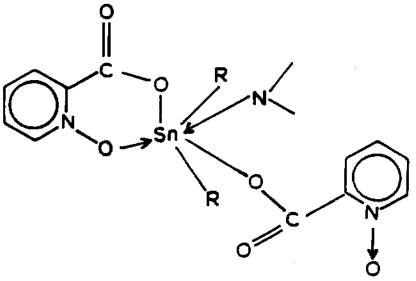
(X= O COC$_5$H$_4$N—2)

III



II

(R = n - C$_4$H$_9$, n - C$_8$H$_{17}$;2:1 Monomer)



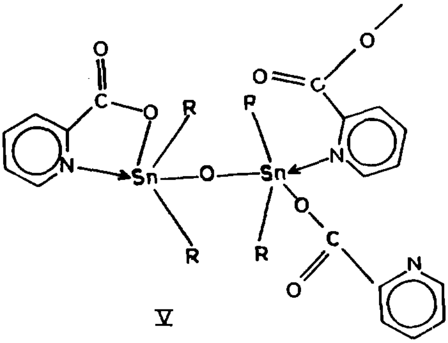
IV

(R=CH$_3$, C$_6$H$_5$CH$_2$; 2:1 Polymer)

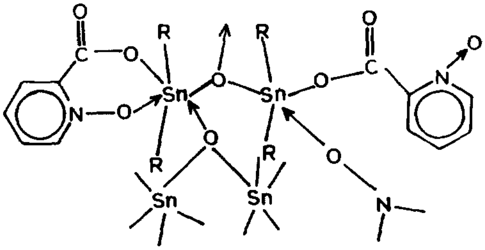
The QS value for complex **3** indicates that it has a regular octahedral structure. In case of the remaining 2 : 1 complexes **9**, **10**, **11** the QS values support a distorted non-linear octahedral structure [6,10]. The 1 : 1 complex **6**. $[Bu_2Sn(Pic)]_2O$, has an IS value of 1.30 and a QS value of 3.33, which fall in the range of a *trans* five-coordinate complex [6,10]. The remaining 1 : 1 dinuclear complexes of picolinic *N*-oxide, **13**, **14**, **15** show two different values of the Mössbauer parameters, falling in the range of five- and six-coordinated tin atoms present in the same molecule. The possibility of a mixture of 2 : 1 and a 1 : 1 complexes is excluded from the elemental analyses; in these 1 : 1 complexes tin(IV) is therefore present in two different environments in the same molecule with an Sn–O–Sn bridge.

Conclusion

On the basis of molecular weight determination, IR and Mössbauer data structures have been proposed for all the complexes. The 2 : 1 complexes have distorted *trans* octahedral structures I–IV with intra- and intermolecular coordination from



V



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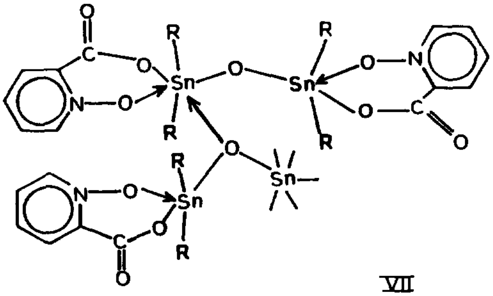

VII

the ring nitrogen in picolinic acid complexes and from *N*-oxide oxygen in the picolinic *N*-oxide acid complexes. However, the carboxylate group coordinates unidentately. The 1 : 1 complex $[Bu_2SnPic]_2O$ has a five-coordinate *trans* trigonal bipyramidal structure V with ring nitrogen coordination to tin(IV) and a unidentate carboxylate. The remaining 1 : 1 complexes of picolinic acid possess structures such as V with inter- or intramolecular coordination from nitrogen to tin(IV). Structures VI and VII are suggested for the 1 : 1 complexes of picolinic acid *N*-oxide in which the Sn–O–Sn bridged oxygen is tricoordinated. The presence of such an oxygen has recently been shown by X-ray studies in other complexes, $\{[R_2SnO_2CCH_2SPh]_2O\}_2$ ($R = {}^nPr$, ${}^nBu$) also [14].

References

1 D.A. Kochkin, S.G. Vereniktha and I.B. Chekmareva, Doklady Akad. Nauk SSSR, 139 (1961) 1375.
2 D.W. Allen, J.S. Brooks, R. Formstone, A.J. Crowe and P.J. Smith, J. Organomet. Chem., 156 (1978) 359.
3 A.J. Crowe, R. Hill, P.J. Smith, J.S. Brooks and R. Formstone, J. Organomet. Chem., 204 (1981) 47.
4 N.V. Datta and C. Columba, Inorg. Chem., 10 (1971) 1017.
5 I.W. Nowell, J.S. Brooks, G. Beech, R. Hill, J. Organomet. Chem., 244 (1983) 119.
6 G.K. Sandhu, R. Gupta, S.S. Sandhu and R.V. Parish, J. Organomet. Chem., 311 (1986) 281.
7 G.K. Sandhu, G. Kaur, J. Holecek and A. Lycka, J. Organomet. Chem., 332 (1987) 75.
8 A.B.P. Lever, J. Lewis and R.S. Nyholm, J. Chem. Soc., (1962) 5262.
9 T. Tanaka, M. Komura, Y. Kawasaki and J. Okarvara, J. Organomet. Chem., 1 (1964) 484.
10 G.K. Sandhu, R. Gupta, S.S. Sandhu, R.V. Parish and K. Brown, J. Organomet. Chem., 279 (1985) 373.
11 J.P. Ashmore, T. Chivers, K.A. Kerr and J.H.G. VonRoode, Inorg. Chem., 16 (1977) 191.
12 R.V. Parish, Prog. Inorg. Chem., 15 (1972) 101.
13 R.V. Parish and C.E. Johnson, J. Chem. Soc. A, (1971) 1906.
14 G.K. Sandhu, N. Sharma and E.R.T. Tiekink, J. Organomet. Chem., 403 (1991) 119.