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THE REACTIONS OF DIALKYLTIN DIISOPROPOXIDES WITH 1-NITROSO-2-NAPHTHOL

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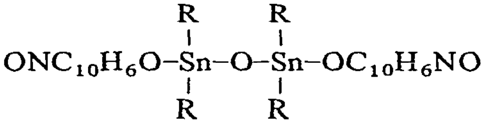
SUMMARY

Reactions of dialkyltin isopropoxides with 1-nitroso-2-naphthol in presence of aqueous ammonia give tetraalkyl-1,3-bis(1-nitroso-2-naphthoxy)distannoxanes.

There are only a few reports on complexes formed by reaction of organotin halides with bidentate chelating agents; these refer to use of dithizone[1,2], 8-hydroxyquinoline[3-5], 1,10-phenanthroline and 2,2'-bipyridine[5-7], acetylacetone and picolinic acid[8], and 1-nitroso-2-naphthol[9].

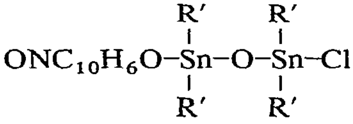
Okawara *et al.*[9] found that dimethyl and diethyltin dichlorides react with 1-nitroso-2-naphthol in methanol in presence of ammonia to form tetraalkyl-1,3-bis(1-nitroso-2-naphthoxy)distannoxanes. However with di-n-propyl- and di-n-butyltin dichlorides, the corresponding tetraalkyl-1-(1-nitroso-2-naphthoxy)-3-chlorodistannoxanes were obtained.



$$ONC_{10}H_6O-\underset{R}{\overset{R}{Sn}}-O-\underset{R}{\overset{R}{Sn}}-OC_{10}H_6NO$$

(I)

($R=CH_3$ and C_2H_5)



$$ONC_{10}H_6O-\underset{R'}{\overset{R'}{Sn}}-O-\underset{R'}{\overset{R'}{Sn}}-Cl$$

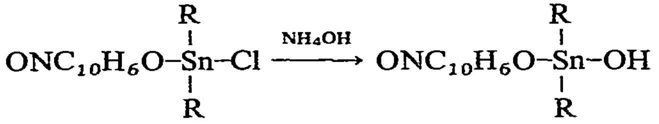
(II)

($R'=n\text{-}C_3H_7$ and $n\text{-}C_4H_9$)

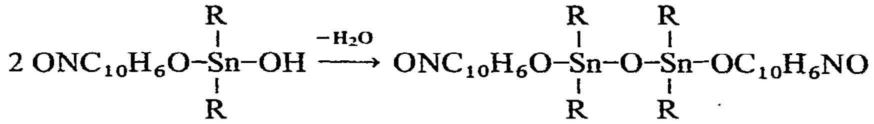
The formation of monochlorodistannoxane products (II) in Okawara's synthesis raises the question of why the terminal chlorine atom does not react with another mole of ligand.

Possible mechanisms for the formation of tetramethyl- and tetraethyl-1,3-bis(1-nitroso-2-naphthoxy)distannoxanes in aqueous solution would involve either:

(*a*) the partial hydrolysis of dialkyltin monochloride (1-nitroso-2-naphthoxide) followed by condensation in the presence of NH_4OH:

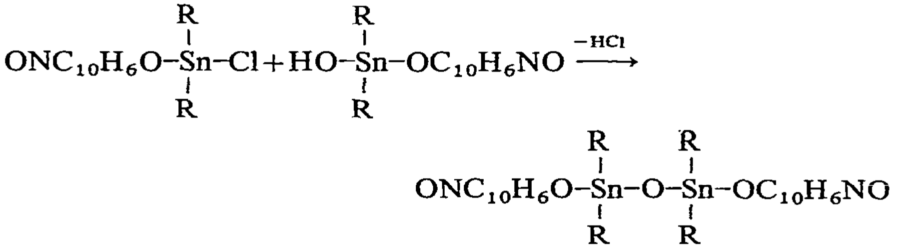


$$ONC_{10}H_6O\text{-}\overset{R}{\underset{R}{Sn}}\text{-}Cl \xrightarrow{NH_4OH} ONC_{10}H_6O\text{-}\overset{R}{\underset{R}{Sn}}\text{-}OH \qquad (1)$$



$$2\,ONC_{10}H_6O\text{-}\overset{R}{\underset{R}{Sn}}\text{-}OH \xrightarrow{-H_2O} ONC_{10}H_6O\text{-}\overset{R}{\underset{R}{Sn}}\text{-}O\text{-}\overset{R}{\underset{R}{Sn}}\text{-}OC_{10}H_6NO \qquad (2)$$

or (*b*) the condensation of dialkyltin monochloride (1-nitroso-2-naphthoxide) with dialkyltin monohydroxide (1-nitroso-2-naphthoxide):



$$ONC_{10}H_6O\text{-}\overset{R}{\underset{R}{Sn}}\text{-}Cl + HO\text{-}\overset{R}{\underset{R}{Sn}}\text{-}OC_{10}H_6NO \xrightarrow{-HCl} ONC_{10}H_6O\text{-}\overset{R}{\underset{R}{Sn}}\text{-}O\text{-}\overset{R}{\underset{R}{Sn}}\text{-}OC_{10}H_6NO \qquad (3)$$

The above anomalous behaviour prompted us to reinvestigate the above system. With dimethyltin and diethyltin dichlorides, the products are of type (I), as reported by Okawara. With n-dibutyltin dichloride, however, the product is still of the type (I), contrary to Okawara, who reported that (II) was formed. In order to substantiate the suggested mechanism of formation of these products (I), $(C_4H_9)_2$-$Sn(OR)OH$ was synthesised by hydrolysis of $(C_4H_9)_2Sn(OR)O$-iso-Pr (where $R=$ 1-nitroso-2-naphthyl). The hydroxy product did not lose water even on heating under vacuum upto 80° ; but did condense with a molecule of $(C_4H_9)_2Sn(OR)Cl$ in the presence of triethylamine to give products of the type (I). This lends support to mechanism (*b*) suggested above.

Mehrotra and coworkers have studied the reactions of dialkyltin(IV) alkoxides with bidentate ligands[10–12] and found that dialkyltin(IV) alkoxides react readily and exothermally with glycols and ethanolamines giving dialkyltin glycollates and aminoethoxides, respectively, in good yields. In view of this straightforward behaviour, the reactions of dialkyltin diisopropoxides with 1-nitroso-2-naphthol in the molar ratios of 1/1 and 1/2 have been studied in dry benzene (Table 1). The isopropanol liberated is estimated by usual procedure[13]. The expected products $R_2Sn(OR)O$-iso-Pr and $R_2Sn(OR)_2$ are obtained. The hydrolytic behaviour of $R_2Sn(OR)O$-iso-Pr has also been studied in hot and cold medium of benzene in presence of water (Table 2). In both the cases identical products dialkyltin hydroxide (1-nitroso-2-naphthoxide) are obtained. No further reaction leading to the formation of tetraalkyl-1,3-bis(1-nitroso-2-naphthoxy)distannoxanes has been observed.

TABLE 1

PREPARATION AND ANALYSIS OF DIALKYLTIN DERIVATIVES OF 1-NITROSO-2-NAPHTHOL

No.	Wt. of alkoxide (g)	Wt. of ligand (g)	Molar ratio	Yield (g)	Colour	Amount of iso-propanol estimated (g)		Analysis found (calcd.) (%)	
						Found	Calcd.	Sn	N
$(CH_3)_2Sn(O\text{-}iso\text{-}Pr)_2$									
1	2.54	3.30	1/2	5.21	Greenish yellow	1.600	1.628	23.77 (24.08)	8.54 (8.74)
2	3.41	2.21	1/1	4.50	Blue	0.686	0.770	30.90 (31.22)	3.64 (3.68)
$(C_2H_5)_2Sn(O\text{-}iso\text{-}Pr)_2$									
3	4.52	5.31	1/2	8.33	Greenish yellow	1.458	1.511	22.72 (22.73)	5.31 (5.36)
4	4.67	2.74	1/1	6.66	Blue	0.740	0.755	28.92 (29.09)	3.41 (3.43)
$(C_4H_9)_2Sn(O\text{-}iso\text{-}Pr)_2$									
5	1.21	1.20	1/2	1.82	Greenish yellow	0.392	0.436	20.45 (20.69)	4.80 (4.88)
6	2.11	1.04	1/1	2.52	Blue	0.331	0.362	25.13 (25.55)	2.98 (3.01)

TABLE 2

CONTROLLED HYDROLYSIS OF DIALKYLTIN MONOISOPROPOXIDE 1-NITROSO-2-NAPHTHOXIDES

No.	Wt. of compound (g)	Hot hydrolysis / Cold hydrolysis	Amount of isopropanol estimated in ternary azeotrope (g)		Analysis found (calcd.) (%)	
			Found	Calcd.	Sn	N
$(CH_3)_2Sn(OC_{10}H_6NO)O\text{-}iso\text{-}Pr$						
1	1.00	Hot	0.153	0.158	35.60 (35.80)	4.10 (4.14)
2	2.10	Cold			34.45 (35.80)	4.02 (4.14)
$(C_2H_5)_2Sn(OC_{10}H_6NO)O\text{-}iso\text{-}Pr$						
3	0.42	Hot	0.062	0.062	32.38 (32.45)	3.67 (3.82)
4	0.40	Cold			32.00 (32.45)	3.68 (3.82)
$(C_4H_9)_2Sn(OC_{10}H_6NO)O\text{-}iso\text{-}Pr$						
5	2.33	Hot	0.181	0.189	28.53 (28.73)	3.27 (3.38)
6	3.21	Cold			28.13 (28.73)	3.30 (3.38)

EXPERIMENTAL

Moisture was rigorously excluded where necessary. Molecular weights were determined with a semi-micro ebulliometer (Gallenkamp) with thermistor sensing (Table 3). IR spectra were recorded with Perkin–Elmer 337 using Nujol as mulling agent. Solvents were dried by the standard procedures. Dimethyl-, diethyl- and dibutyltin diisopropoxides were prepared by the sodium method, and will be discussed elsewhere[14].

TABLE 3

PROPERTIES OF DIALKYLTIN DERIVATIVES OF 1-NITROSO-2-NAPHTHOL

No.	Nature of the compound	Melting behaviour	Mol. wt.		Molecular complexity
			Found	Calcd.	
1	$(CH_3)_2Sn(OC_{10}H_6NO)_2$	Shrinks at 178° and decomposed between 210–215°	541	493	1.0
2	$(CH_3)_2Sn(O\text{-iso-Pr})(OC_{10}H_6NO)$				
3	$(C_2H_5)_2Sn(OC_{10}H_6NO)_2$	Shrinks at 160° and decomposed at 180°	526	521	1.0
4	$(C_2H_5)_2Sn(O\text{-iso-Pr})(OC_{10}H_6NO)$				
5	$(C_4H_9)_2Sn(OC_{10}H_6NO)_2$	104–105°	580	577	1.0
6	$(C_4H_9)_2Sn(O\text{-iso-Pr})(OC_{10}H_6NO)$				
7	$[(C_2H_5)_2Sn(OC_{10}H_6NO)]_2O$	Decomposed above 205°	715	713	1.0
8	$[(C_4H_9)_2Sn(OC_{10}H_6NO)]_2O$	Decomposed above 208°	850	826	1.0

Analysis

Tin in these compounds was estimated as SnO_2 by rupturing the metal–carbon σ bond with fuming nitric acid and fuming sulphuric acid in a silica crucible and then igniting to give a constant weight of SnO_2.

Nitrogen in these compounds was prereduced with zinc dust and hydrochloric acid in methanol to convert –NO group to $-NH_2$ group and then estimated by the usual Kjeldahl procedure.

Preparation of tetrabutyl-1,3-*bis*(1-*nitroso*-2-*naphthoxy*) *distannoxane*

Dibutyltin dichloride (3.03 g) was treated with 1-nitroso-2-naphthol (3.46 g) in the molar ratio 1/2 in the presence of excess of diluted ammonia (10 ml, 1 *N*). Heating on a hot plate with vigorous stirring for three h gave a black product $[(C_{10}H_6NO_2)Sn(C_4H_9)_2]_2O$ which was filtered and dried. (Found: N, 3.35; Sn, 28.35. $C_{36}H_{48}N_2O_5Sn_2$ calcd.: N, 3.38; Sn, 28.75%.)

An alternative route for the preparation of tetrabutyl-1,3-bis(1-nitroso-2-naphthoxy)distannoxane was also used. Dibutyltinmono(1-nitroso-2-naphthoxy)tin hydroxide, prepared by the hot hydrolysis of mono(1-nitroso-2-naphthoxy)dibutyltin isopropoxide, reacts with mono(1-nitroso-2-naphthoxy)dibutyltin chloride, prepared by adding stoichiometric amount of triethylamine in benzene to dibutyltin dichloride and 1-nitroso-2-naphthol (1/1) in refluxing benzene using $(C_2H_5)_3N$ as proton acceptor. The refluxing is continued for an hour and the precipitate formed is filtered to separate $(C_2H_5)_3NHCl$. Excess benzene is removed by normal distillation and the remainder is removed *in vacuo* at 80°. The elemental analysis corresponds to $[(C_4H_9)_2$-$Sn(C_{10}H_6NO_2)]_2O$.

RESULTS AND DISCUSSION

The IR spectra of various derivatives of dialkyltin(IV) with 1-nitroso-2-naphthol are shown in Table 4 along with some tentative band assignments[15]. However, a few absorptions which throw light on the structure of the compounds are discussed below.

3400–3200 *cm*$^{-1}$

Only two compounds namely mono(1-nitroso-2-naphthoxy)diethyl and mono-(1-nitroso-2-naphthoxy)dibutyltin hydroxides (G and H) show a broad absorption in this region showing thereby the presence of hydroxyl group. The limited solubilities of these compounds in C_6H_6, $CHCl_3$ and CCl_4 precludes solution spectral studies for obtaining additional information regarding hydrogen bonding and bridging behaviour of –OH group.

1650–1400 *cm*$^{-1}$

In the unchelated ligand a peak around 1625 cm^{-1} has been assigned to the stretching vibration of N=O. Any bonding to metal either through nitrogen or oxygen is expected to shift this absorption to lower wave numbers. However, according to Leden–Chatt classification[16] dialkyltin(IV) should, like tin(IV) lie on the borderline between these two classifications *i.e.* A and B types of acceptors. Most of the available evidence suggests that it is a type A acceptor[17–20]. It is thus believed that in the present complexes a shift of about 25–30 cm^{-1} in the 1625 cm^{-1} absorption towards lower wave number is a good indication of chelate formation involving oxygen of the nitroso group with dialkyltin(IV) atom. This is further supported by the fact that ν(CNO) which is observed at 1375 cm^{-1} vw is not shifted (except in F, G, H and J) during coordination. The shifts in F, G, H and J may be due to the considerable overlap of $\delta[(CH_3)(Sn-CH_3)]$ or $\delta[(CH_2)(Sn-CH_2)]$, which also give rise to bands in this same region, with the characteristic vibrations of isopropoxy group which has an absorption band at 1375 cm^{-1}. The other vibrations are due to aromatic ring, C=C, C–O, and δ(C–H), respectively.

1400–1300 *cm*$^{-1}$

Besides the deformation vibration of methyl and methylene groups this region shows characteristic peaks arising from the *gem*-dimethyl group. A peak of medium to strong intensity at 1375 cm^{-1} is observed in dimethyltin diisopropoxide (A), dimethyltin monoisopropoxide (1-nitroso-2-naphthoxide) (B) and dibutyltin monoisopropoxide (1-nitroso-2-naphthoxide) (C), whereas Mazdiyasni has reported a doublet at about 1375 and 1365 cm^{-1} in the transition metal isopropoxides.

1300–700 *cm*$^{-1}$

All the compounds containing isopropoxy groups show skeletal vibrations

(*Continued p.* 136)

TABLE 4

INFRARED SPECTRA OF THE DERIVATIVES OF DIALKYLTIN WITH 1-NITROSO-2-NAPHTHOL (cm^{-1})[a]

A	B	C	D	E	F	G	H	I	J	K	Assignment
						3400–3300 (b)	3400–3200 (b)				$\nu_{as}(\mathrm{O{-}H})$
			3170 vs								$\nu_{as}(\mathrm{C{-}H})$ Nujol
3100 vs	3100 vs		3125 vs								
	3080 m	2970 (sh)	3050 m					2980 vs	2970 vs	3080 vs	$\nu_{s}(\mathrm{C{-}H})$ Nujol
3040 vs	3040 m	2940 s	2940 vs	2950 (b)	2950 vs	2975 vs	2950 s	2920 (b)	2940 w	2940 s	
2880 m		2860 w	2860 w	2850 (b)	2850 vs	2940 vs	2850 s	2875 w	2860 (sh)	2875 m	$\nu_{as}(\mathrm{C{-}H})$
											$\nu_{s}(\mathrm{C{-}H})$
1950 vs	1950 vs										Combination and overtone
1810 vs	1810 vs										
		1590 m	1620 vs	1600 s	1600 s		1600 s	1620 s	1600 m	1625 s	$\nu(\mathrm{N{=}O})$
	1600 m		1595 m	1590 m	1590 w	1590 m	1595 m				
1575 w	1570 w		1570 m					1580 m	1580 w	1580 m	$\Phi_{ring}+\nu(\mathrm{C{=}C})+\nu(\mathrm{C{-}O})$
1520 w	1520 s	1560 s	1560 w	1545 m	1540 m				1575 w	1560 w	
			1500 w	1500 w (b)	1500 w			1550 s	1560 w	1525 s	
1470 vs		1470 s	1455 s	1450 s	1450 s		1540 m		1540 w		
1425 m			1400 s			1450 vs	1500 m		1500 m		$\nu(\mathrm{C{=}C})+\delta(\mathrm{C{-}H})+\nu(\mathrm{C{-}CH_3})$
							1490 m			1450 s	$+\nu(\mathrm{C{-}CH_2})+\Phi_{ring}$
							1450 s	1460 vs	1445 s	1400 s	
1375 m	1375 s	1375 s	1375 s	1375 s	1370 s	1370 s	1360 m	1375 vs	1360 s	1375 vw	$\nu(\mathrm{CNO})+\delta_{as}(\mathrm{CH_3})$ or
			1340 s	1340 w	1340 w		1300 w	1340 w			$(\mathrm{Sn{-}CH_2})$ group
			1310 m	1296 m				1300 w	1325 w	1325 s	$+\delta\left(\mathrm{CH}\begin{smallmatrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{smallmatrix}\right)$
			1290 w				1280 m		1285 m		

		1265 m	1265 w	1265 s			1264 m		1261 w	1263 s	
				1245 m (sh)				1255 w }D			Φ_{ring} 1,2-substitution + ν(C–O)
	1248 m		1245 vs		1238 m		1240 m	1245 w }	1235 m		
							1220 m				
			1220 s	1218 m	1215 m		1200 w	1220 s	1215 m	1218 s	
		1208 w	1180 s	1180 m			1190 m	1180 m	1170 vw	1160 m	
1173 m	1175 s	1185 w			1160 w	1150 w	1160 w	1160 m	1150 m	1145 m	
	1145 sh	1150 m	1150 s	1156 m			1150 w	1140 m			$\nu(C{-}O)+\nu\left(C\ddot{H}\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\right)$
1143 w	1093 w		1095 s }D	1080 w	1075 w	1085 w	1085 m	1080 m	1085 m	1098 w	
		1070 m	1085 s }			1000 m	1030 m	1020 m	1070 m (b)	1073 vs	
1031 vs	1040 vs	1045 w	1020 w	1012 w	1018 m		1010 m			1030 w	
		1025 w									
		1005 m									
	985 (sh)	978 m	985 w				990 m			998 m	π(C–H) + $\rho_r(CH_3)$
			950 w	950 w		975 w (b)				968 s	
				885 w		895 w	870 m	870 m		883 w	+ $\rho_r(CH_2)$
		878 w	870 w	870 m	870 w	875 w	813 s	840 s	825 m	853 vs	
843 m	845 m	855 w			835 s			813 w		783 s	
		815 w	832 s	830 s		795 w	800 s	785 w			
		795 s									
768 m	768 m		768 s				745 s			763 s }D	π(CH) + ν_{as}(Sn–O–Sn)
723 w	723 m	738 s	750 w	750 vs	750 s	740 s		755 s	750 m	753 m }	
		715 w	720 w					720 w		713 s	
			695 w	680 m	670 m	665 m	670 w	675 m	670 m	688 s	ν_{as}(Sn–O)
650 vs (b)	670 vs (b)	670 m		660 w		640 m	648 w			645 m	
			635 s	630 s	630 m		615 m	635 s	625 m		ν_s(Sn–O)
593 w	593 w	590 m	590 m	590 w							
550 (sh)		550 m	575 m	570 m	570 w	560 m	555 w	575 m	565 w		ν(Sn–C), ν(Sn–O)
523 w	530 w		528 w	550 w		525 w	540 m	555 w	555 w	528 m	+ Φ_{ring} vibration
500 w				520 m	515 w		480 m	510 m	510 m	521 m	
485 w	482 w	488 w	495 w	505 w	440 w	480 (sh)	450 m	490 vw	495 w	493 vs	
460 w	420 w (sh)	435 w (b)	450 (sh)	430 (sh)		465 (sh)	420 m	430 w			

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[a] A = $(CH_3)_2Sn(O\text{-iso-}Pr)_2$; B = $(CH_3)_2Sn(OR)O\text{-iso-}Pr$; C = $(C_4H_9)_2Sn(OR)O\text{-iso-}Pr$; D = $[(CH_3)_2SnOR]_2O$; E = $[(C_2H_5)_2SnOR]_2O$; F = $[(C_4H_9)_2SnOR]_2O$; G = $(C_2H_5)_2Sn(OR)OH$; H = $(C_4H_9)_2Sn(OR)OH$; I = $(C_4H_9)_2Sn(OR)_2$; J = $(C_2H_5)_2Sn(OR)_2$; K = 1-nitroso-2-naphthol (ROH).

between 1125–1175 cm^{-1}. There is ample evidence in the literature for this absorption[21,22]. These vibrations are assigned to isobranching vibrations of the isopropoxy group in compounds A, B and C respectively. Mazdiyasni[21], however, reported the region 1160–1175 cm^{-1} and 1120–1140 cm^{-1}, for the skeletal vibrations in the transition metal isopropoxides, whereas Barraclough[22] *et al.* ascribed the band at 1030 cm^{-1} to bridging ethoxide groups as these are found to disappear leaving the rest of the spectrum unaltered on partial hydrolysis of the compounds. Thus the position of the ν(C–O) band could vary from 950–1070 cm^{-1} depending upon the metal atom. Bell and co-workers[23] have found characteristic absorptions, for the isopropoxides of non-transition elements, *viz.* B, Al and P, in the range 1170–1176 cm^{-1}, 1134–1139 cm^{-1} and 1110–1124 cm^{-1}, and assigned these to the skeletal vibrations of isopropoxy groups.

The bands in region 900–700 cm^{-1} are assigned to $PrCH_3$, $PrCH_2$ and π(C–H) respectively.

700–400 *cm*$^{-1}$

In almost all the compounds three strong to medium intensity peaks around 650, 635–630, and 595 cm^{-1} have been observed. The origin of these peaks is believed to be due to Sn–O–Sn and Sn–O stretching vibrations. In case of dimethyltin dimethoxide[24,25] two peaks at 644 and 609 cm^{-1} have been assigned to asymmetric and symmetric vibrations of Sn–O. It seems logical, therefore, to assume that the absorptions at 640 and 595 cm^{-1} can be assigned to the antisymmetric and symmetric vibrations of the Sn–O bond.

Okawara and coworkers[26–28] have reported a band at 650 cm^{-1} associated with ν(Sn–O–Sn), whereas Kriegsmann *et al.*[29] has reported the same absorption at 740 cm^{-1}. Such disagreement may be due to the fact that only methyl derivatives of tin have been studied and of rotational and vibrational absorptions of CH_3 groups may be overlapping to some extent with the asymmetric vibrations of Sn–O–Sn. This is supported by the work of Trezbiatowsa and coworkers[30] who have studied the fluoro and hydroxyfluoro derivatives of tin as well as the thermally condensed bi- and polynuclear products, and found two bands in non-condensed products in the region 750–700 cm^{-1} and 624–615 cm^{-1}, which they assigned to Sn–O stretch, whereas in condensed products they assigned a band between 750–780 cm^{-1} to ν_{as}(Sn–O–Sn), and a band between 465–490 cm^{-1} to ν_s(Sn–O–Sn), contained in linear, ring and cross-linked structures. On the basis of these observations we believe that the peaks at 635 cm^{-1} are due to ν_{as}(Sn–O–Sn) and a peak which appears at 750 cm^{-1} is either due to bending mode of methyl group or a combination of the above with assymetric stretch of Sn–O–Sn. The symmetric stretch of Sn–O–Sn is, however, very difficult to locate due to the weak nature of the spectrum in the 400 cm^{-1} region.

A number of authors have used ν(Sn–C) in elucidating the structure of tin compounds[29]. McGrady and Tobias[30] used Raman studies to prove the presence of linear structure of $(CH_3)_2Sn^{++}$ in aqueous and non-aqueous solutions. Clark and Wilkins[31] proved the existence of five- and six-coordinated tin on the basis of different number of absorptions observed in these cases. However, it is difficult to draw any such conclusion in the present investigations, since a number of weak absorptions are observed below 500 cm^{-1} and these could have their origin in Sn–C or Sn–O or ring vibrations.

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REFERENCES

1 W. N. Aldridge and J. E. Cremer, *Analyst (London)*, 82 (1957) 37.
2 H. Irving and J. J. Cox, *J. Chem. Soc.*, (1961) 1470.
3 D. Blake, G. E. Coates and J. M. Tate, *J. Chem. Soc.*, (1961) 756.
4 L. Ronucci, G. Faraglia and R. Barbieri, *J. Organometal. Chem.*, 1 (1964) 427.
5 I. Tanaki, M. Komura, Y. Kawasaki and R. Okawara, *J. Organometal. Chem.*, 1 (1964) 484.
6 D. L. Alleston and A. G. Davis, *J. Chem. Soc.*, (1962) 2050.
7 I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, (1963) 1519.
8 M. J. Yasuda and R. S. Tobias, *Inorg. Chem.*, 2 (1963) 207.
9 T. Tanaka, R. Ue-eda, M. Wada and R. Okawara, *Bull. Chem. Soc. Jap.*, 37 (1964) 1554.
10 V. D. Gupta, Ph.D. Thesis, Rajasthan University, Jaipur, 1965.
11 R. C. Mehrotra and V. D. Gupta, *J. Organometal. Chem.*, 4 (1965) 145.
12 R. C. Mehrotra and V. D. Gupta, *J. Organometal. Chem.*, 4 (1965) 237.
13 R. C. Mehrotra, *J. Indian Chem. Soc.*, 31 (1954) 904.
14 R. C. Mehrotra and B. P. Bachlas, *J. Organometal. Chem.*, 22 (1970) 121.
15 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen Press, London, 1966.
16 S. Ahrland, J. Chatt and N. R. Davis, *Quart. Rev. (London)*, 12 (1958) 723.
17 C. J. Wilkins and H. M. Haendler, *J. Chem. Soc.*, (1965) 3174.
18 A. A. Woolf, *J. Inorg. Nucl. Chem.*, 3 (1956) 285.
19 E. L. Muetterties, *J. Amer. Chem. Soc.*, 82 (1960) 1082.
20 M. Yasuda and R. S. Tobias, *Inorg. Chem.*, 2 (1963) 207.
21 C. T. Lynch, K. S. Mazdiyasni, J. S. Smith and W. J. Crawford, *Anal. Chem.*, 36 (1964) 2332.
22 C. G. Barraclough, D. C. Bradley, J. Lewis and I. M. Thomas, *J. Chem. Soc.*, (1961) 2601.
23 J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *Anal. Chem.*, 25 (1953) 1720.
24 N. N. Vyshinskii and N. Rudenskii, *Opt. Spectrosk.*, 10 (1961) 421.
25 F. K. Batchev, W. Gerrard, E. F. Mooney, R. G. Rees and H. A. Willis, *Spectrochim. Acta*, 20 (1964) 51.
26 R. Okawara, Y. Kawasaki and T. Tanaka, *VIIth Int. Conf. on Coordination Chemistry*, 17C5, Vienna, Sept. 1964.
27 R. Okawara, M. Wada, R. Ue-eda and T. Tanaka, *Bull. Chem. Soc. Jap.*, 37 (1964) 1554.
28 M. P. Brown, R. Okawara and E. G. Rochow, *Spectrochim. Acta*, 16 (1960) 595.
29 R. Okawara and M. Wada, in F. G. A. Stone and R. West (Eds.), *Advances in Organometallic Chemistry*, Vol. 5, Academic Press, 1967, p. 137.
30 M. M. McGrady and R. S. Tobias, *Inorg. Chem.*, 3 (1964) 1157.
31 J. P. Clark and C. J. Wilkins, *J. Chem. Soc. A*, (1966) 871.