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FIVE-COORDINATE COMPLEXES OF 2,2-DIBUTYL-1,3,2-DIOXASTANNOLANS

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Summary

2,2-Dibutyl-1,3,2-dioxastannolans, $Bu_2Sn(OCR_2)_2$, unlike the dioxastannanans, $Bu_2Sn(OCR_2)_2CR_2$, or the acyclic dialkoxides, $Bu_2Sn(OR)_2$, react with ligands L, such as pyridine, dimethyl formamide, dimethyl sulphoxide, sulpholane, and tetrahydrofuran to form a series of solid complexes, $Bu_2Sn(OCR_2)_2L$. Under reduced pressure, the ligands, L, are lost, and the dioxastannolans are regenerated. Measurements of IR, ^1H and ^{119}Sn NMR, and Mössbauer spectra, and of molecular weights in solution, imply that the complexes have a trigonal bipyramidal configuration, with equatorial butyl groups, apical ligand L, and the dioxastannolan ring bridging apical and equatorial positions. It is suggested that the relative stability of these complexes results from minimisation of angle strain in the 5-membered ring.

Introduction

The principal factor which controls the ability of a tin(IV) compound to increase its coordination number above 4 is the electronegativity of the ligands [1]. Thus tetraalkyltins, R_4Sn, show no tendency to be more than 4-coordinate, but trialkyltin(IV) compounds R_3SnX, where X is a ligand more electronegative than carbon, frequently form 5-coordinate complexes. The first to be established crystallographically was Me_3SnCl,py, in which the three alkyl groups are equatorial, and the remaining two groups apical, in a trigonal bipyramid [2]. Similar structures occur by self-association; for example, trimethyltin fluoride in the crystal is a linear polymer with bridging fluorine, and approximate C_{3v} symmetry about the tin [3]. Apart from X-ray crystallography [4], ^{119m}Sn Mössbauer spectroscopy (particularly the quadrupole coupling parameter) of solids [5], and ^{119}Sn NMR spectroscopy (particularly the chemical shift parameter) of liquid samples [6] have been widely used as criteria of coordination numbers [1].

Dialkyltin(IV) compounds, R_2SnX_2, are more prone than trialkyltin(IV) compounds, R_3SnX, to increase their coordination numbers, and numerous 5- and 6-coordination complexes are known. Self-association, usually to give 5-coordinate

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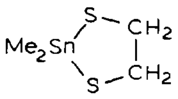
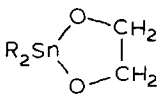
tin, is so common that 4-coordination is the exception rather than the rule [1]. Typical examples of 5- and 6-coordinate complexes of dialkyltin(IV) compounds are Me_2SnCl_2 [7], Me_2SnCl_22py [8], $Me_2Sn(acac)_2$ [9], and $(Me_2SnCl)_2O$ [10].

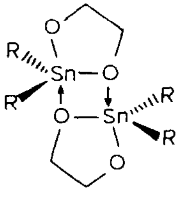
A secondary factor which has been recognised to influence the ability of tin to act as a Lewis acid is that of interbond angles. Thus the dithiastannolan (I), unlike the acyclic analogues, $Me_2Sn(SR)_2$, shows a large upfield ^{119}Sn chemical shift in dimethyl sulphoxide solvent, indicative of coordinative association, and crystalline complexes $R_2Sn(SCH_2)_2$,dmso (R = Me or Ph) can be isolated [11,12].



(I)



(II)



(III)

Similarly, molecular weight measurements of 2,2-dialkyl-1,3,2-dioxastannolans (II) show that they are dimerised in solution [12], and the ^{119}Sn chemical shift is independent of concentration, or whether the compound is molten, whereas acyclic dialkoxides, $R_2Sn(OR')_2$ show ^{119}Sn chemical shifts which fall off if the solutions are diluted or if the temperature is raised, indicating a weaker association [13]. An X-ray diffraction study of the dibutyldioxastannolan derived from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside confirmed the 5-coordinate structure III [14].

Apart from this self-association by the dioxastannolans, there appears to be no previous evidence for the formation of 5-coordinate complexes by the dialkyltin dialkoxides. We report here that the dioxastannolans but not the dioxastannanans or the acyclic dialkoxides will form a series of 5-coordinate complexes with monodentate ligands. A number of these have been isolated and characterised, and examined by NMR and Mössbauer spectroscopy.

The dioxastannolans IV–VII, and the ligands i–v, which were investigated are shown in eq. 1.

(1)

(VIII)

(IV, $R_2 = R'_2 = H_2$;
V, R_2 = H,Me· $R'_2 = H_2$;
VI, $R_2 = R'_2$ = Me, H (*erythro/threo* = 1/2);
VII, $R_2 = R'_2 = Me_2$)

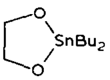
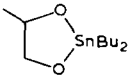
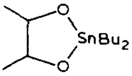
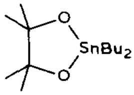
(i, C_5H_5N (py);
ii, Me_2NCHO (dmf);
iii, Me_2SO (dmso);
iv, $(CH_2)_4SO_2$ (sane);
v, $(CH_2)_4O$ (thf))

The complexes with pyridine, dimethyl sulphoxide, and tetrahydrofuran, rapidly separated in high yield when the dioxastannolan was dissolved on warming in the ligand, and the complexes with dimethyl formamide separated when the solution was left to stand overnight. The complexes with sulpholane were obtained by dissolving the distannoxane and sulpholane in warm chloroform, and allowing the solvent to evaporate.

If a complex with water as the ligand could be formed, it would represent the intermediate involved in the hydrolysis of the dioxastannolan. However, treatment of IV in chloroform with water gave a product which was soluble in chloroform, and showed (NMR) the presence of butyl and OH groups but the absence of the diol moiety. The complex with water as a ligand is apparently unstable, and hydrolysis proceeds with loss of the diol to give a soluble hydrated form of dibutyltin oxide, probably the distannoxane $HOSnBu_2OSnBu_2OH$.

TABLE 1

ANALYSES AND ^{1}H NMR SPECTRA OF DIOXASTANNOLAN COMPLEXES

Dioxastannolan	Ligand L	L(%) (Obsvd. (Calcd.))	^{1}H NMR (δ)[a]	
			OCHCHO	L[b]
	(i) py	19.9 (21.3)	3.53	7.14, 7.53, 8.43
	(ii) dmf	19.9 (20.7)	3.65	2.97, 2.87 (Me_2), 8.07 (CHO)
	(iii) dmso	21.5 (21.1)	3.65	2.60 (Me_2)
	(iv) sane	27.1 (29.0)	3.60	2.17 (αCH_2), 3.00 (βCH_2)
	(v) thf	17.8 (19.3)	3.56	3.7 (αCH_2), 1.8 (βCH_2)
	(i) py	22.7 (20.5)	3.60	7.18, 7.60, 8.50
	(ii) dmf	20.0 (18.9)	3.60	2.87, 2.92 (Me_2)
	(iii) dmso	20.8 (20.3)	3.60	2.67 (Me_2)
	(iv) sane	[c]	3.60	2.20 (αCH_2), 2.94 (βCH_2)
	(i) py		3.27	7.20, 7.60, 8.50
	(ii) dmf	16.6[d] 18.6	3.27	2.88, 2.96 (Me_2), 8.07 (CHO)
	(iii) dmso	[e]	3.27	2.60 (Me_2)
	(iv) sane	[f]	3.27	2.20 (αCH_2), 3.00 (βCH_2)
	(iii) dmso		–	2.60 (Me_2)

[a] In $CHCl_3$. All the complexes showed δ 0.8–1.8 for the butyl groups, and the ring methyl groups, when present. [b] Values for the free ligands are (i) 7.20 (m, *m*-H), 7.55(m, *p*-H), 8.60 (m, *o*-H); (ii) 2.90, 2.98 (s, Me_2), 8.01 (s, CHO); (iii) 2.60 (s, Me_2), (iv) 2.25 (m, αCH_2), 3.05 (m, βCH_2), (v) 1.83 (m, αCH_2), 3.71 (m, βCH_2). [c] Found: C, 41.7; H, 7.30. $C_{15}H_{32}O_4SSn$ calcd.: C, 42.2; H, 7.55%. [d] Found: C, 44.1; H, 7.66. $C_{15}H_{33}NO_3Sn$ calcd.: C, 45.7; H, 8.44%. [e] Found: C, 41.1; H, 7.97. $C_{14}H_{32}O_3SSn$ calcd.: C, 42.1; H, 8.08%. [f] Found: C, 44.1; H, 7.76. $C_{16}H_{34}O_4SSn$ calcd.: C, 43.6; H, 7.71%.

TABLE 2

INFRARED AND MÖSSBAUER SPECTRA

Compound	IR (cm^{-1})[a]		Mössbauer ($mm\ s^{-1}$)[b]	
	ν(L)	ν(OSnO)	δ	ΔEq
IV,i	1580	680	0.93	2.23
IV,ii	1660, 1690	665	1.01	2.11
IV,iii	1060	680	1.01	2.12
IV,iv	1070, 1115, 1155, 1310	680	1.11	2.55
IV,v	–	690	1.09	2.64
V,i	1580	690	1.11	2.66
V,ii	1670, 1690	680	1.07	2.47
V,iii	1060	680	0.91	2.21
V,iv	1060, 1120, 1150, 1310	680	0.93	2.39
VI,i	1580	690	0.94	2.22
VI,ii	1695, 1670	690	0.74[c]	2.51[c]
VI,iii	1080	685	0.97	2.13
VI,iv	1030, 1120, 1155, 1310	685	0.96	2.35
VII,iii	1070	680	0.99	2.16
IV	–	680	1.10	2.80
V	–	690	1.13	2.72
VI	–	685	1.25	2.82
VII	–			
i	1580			
ii	1690			
iii	1070			
iv	1115, 1155, 1305			

[a] Nujol mulls. [b] At 90 K, versus SnO_2. [c] Approximate values because of the presence of free dioxastannolan.

In contrast to the behaviour of the dioxastannolans, no complexes could be formed from dibutyltin dimethoxide, or 2,2-dibutyl-1,3,2-dioxastannanan, nor unfortunately, from the dibutyltin derivative of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside.

All the complexes were rather unstable, and all lost the ligand and reverted to the dioxastannolan on standing in the air, and all gave melting points approximating to that of the parent dioxastannolan presumably because the ligand was lost on heating. Some were stable enough for microanalysis to be carried out successfully. Most were authenticated by integrated ^{1}H NMR spectroscopy, and by measuring the loss in weight which occurred when the ligand was removed under reduced pressure (see Table 1). Infrared and Mössbauer spectra are listed in Table 2, and ^{119}Sn NMR chemical shifts and molecular weights in chloroform solution (by vapour pressure osmometry) are given in Table 3.

The quadrupole splitting parameter, ΔEq, in the Mössbauer spectrum indicates the stereochemistry of the ligands about tin in the solid state. The 2,3-*O*-dibutyltin-derivative of methyl-4,6-*O*-benzylidene-α-D-glucopyranoside, which has been shown to have the structure III, has δ 1.14 ppm, ΔEq 2.72 mm s^{-1}, and the dioxolans IV–VII, which we assume to have a similar structure, show ΔEq values lying between 2.72 and 2.82 mm s^{-1} (Table 2). All the complexes showed ΔEq values rather smaller (2.11–2.66 mm s^{-1}; see Table 2) than in the parent dioxastannolans, compatible with preservation of an approximately trigonal bipyramidal structure

TABLE 3

^{119}Sn NMR SPECTRA AND MOLECULAR WEIGHTS

Compound	$\delta(^{119}\text{Sn})$ [a] (ppm)	M		$\frac{2}{3}M$ Calcd.
		Obsvd. [b]	Calcd.	
IV,i	-144.0			
IV,ii	-137.2			
IV,iii	-144.4	310	371	247
IV,iv		294	413	275
V,i	-146.4			
V,iv		339	427	285
VI,i	-145.6			
VI,ii	-144.9	382	394	263
VI,iv		301	441	294
IV	-189			
V	-164			
VI	-155			

[a] In $CDCl_3$ solvent against Me_4Sn as external standard. Upfield shifts are taken as negative. [b] In $CHCl_3$ at 37°C.

with equatorial alkyl groups; indeed this appears to be the only structure that is known for 5-coordinate complexes R_2SnX_3 [4].

The other of the techniques which we have used which can give evidence for the structure in the solid state is infrared spectroscopy of Nujol mulls. The results in Table 2 show that there is little change in the characteristic vibration frequences of either the dioxastannolans or of the ligands when the complexes are formed. This supports the conclusion that the complexing is loose, with little effect on the bonding within the ligand.

The most informative results on solutions of the complexes come from measurements of molecular weights by vapour pressure osmometry (see Table 3). The parent dioxastannolans show molecular weights corresponding to the dimers III, with no significant dissociation. If the complexes dissociated completely in solution as shown in eq. 2, the observed molecular weight should be $\frac{2}{3}$ of that calculated for the complex.

$$2Bu_2Sn(OCR_2)_2L \rightarrow [Bu_2Sn(OCR_2)_2]_2 + 2L \qquad (2)$$

The results in Table 3 suggest that all the complexes are extensively dissociated in solution, the sulpholane complexes in particular being almost completely dissociated. This is supported by the proton magnetic resonance spectra, which are close to those of the free ligands. The ^{119}Sn NMR chemical shift is a good indicator of coordination number, moving to higher field as the coordination number increases. For example, dibutyltin dimethoxide, which associates to a 5-coordinate dimer shows $\delta(^{119}\text{Sn})$ -165 ppm, about 130 ppm upfield from the signal of dibutyltin di-t-butoxide (δ -34 ppm), which, for steric reasons is monomeric.

All the complexes prepared here showed a single ^{119}Sn NMR signal lying between δ -137 and -146, within the range expected for 5-coordinate tin, but rather lower than the values for the parent dioxastannolans. This again would be compatible with the equilibria shown in eq. 2.

We conclude that the dioxastannolans, unlike the dioxastannanans or the acyclic dialkyltin dialkoxides, will form loose *cis* trigonal bipyramidal complexes VIII in the solid state, which are extensively dissociated in solution. Such 5-coordination is unusual in mononuclear organotin complexes, although, as noted above, it is recognised in the corresponding dithiastannolans [11]; 6-coordination to give complexes $R_2SnX_2L_2$ is much more common.

The enhanced coordinating ability of the dioxastannolans (and the dithiastannolans) over that of the corresponding six-membered ring and acyclic compounds probably results from the relative angle strain in the 5-membered ring when it includes a 4-coordinate rather than a 5-coordinate tin atom. A Dreiding model of a dioxastannolan (II) shows that it is severely strained, but that this strain is relieved when the tin is made 5-coordinate so that the ring bridges apical and equatorial positions in complexes VIII. A similar interpretation was proposed by David, Pascard and Cesario to account for the ready formation of the dimers III [14].

A similar general effect might be expected in other metallolans where the metal has a large covalent radius but such a phenomenon does not appear to be recognised.

Experimental

The dioxastannolans were prepared by azeotropic dehydration of a mixture of dibutyltin oxide and the diol.

Mössbauer spectra were recorded at the International Tin Research Institute, or through the University of London Intercollegiate Research Service at Birkbeck College. The samples were cooled in liquid nitrogen, and isomer shifts are quoted against SnO_2 as standard.

Molecular weights were determined in chloroform solution at 37°C using a Hewlett Packard Vapour Pressure Osmometer Model 302. Values quoted are the average of two measurements in the range 3.8–7.2 g dm^{-3}.

^{119}Sn NMR spectra were recorded on a Varian XL 200 spectrometer using Me_4Sn in deuterioacetone as external standard.

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