

Tin(IV) and organotin(IV) adducts of bis(3,5-dimethylpyrazol-1-yl)methane or of 2,2'-bis(pyrazol-1-yl)propane and their behaviour in solution

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Abstract

Adducts of bis(3,5-dimethylpyrazol-1-yl)methane or 2,2'-bis(pyrazol-1-yl)propane with tin(IV), trimethyl-, or triphenyl-tin(IV) halides as well as of the former ligand with diphenyl-, or dimethyl-tin(IV) halides have been isolated and characterized. Solution data (¹H, ¹³C, ¹¹⁹Sn NMR spectra, conductivity measurements and molecular weight determinations) show that the adducts from the less acidic acceptors [(Me₂pz)₂CH₂]₃(Me₂SnCl₂)₂ and [(Me₂pz)₂CH₂]Ph₂SnCl₂ undergo extensive dissociation.

Introduction

There is growing interest in the coordination behaviour of bis(pyrazol-1-yl)alkanes, a family of stable and flexible ligands [1]. However, few papers have appeared on the non-transition metal derivatives of this class of ligands, and we decided to undertake an investigation in this area [2a,2b,3a,3b,3c,4]. Previously, we described derivatives of bis(3,5-dimethylpyrazol-1-yl)methane, (Me₂pz)₂CH₂ or L–L, with zinc, cadmium [2a], and mercury(II) or mercury(I) [2b]. Here we describe the results of studies of the interaction of organotin(IV) compounds, R_{4–n}SnX_n (R = methyl or phenyl; X = Cl, Br; n = 0–4), with the same ligand as well as with the related 2,2'-bis(pyrazol-1-yl)propane (Pz)₂CMe₂ or L'–L', in order to extend the results previously obtained with bis(pyrazol-1-yl)methane, (Pz)₂CH₂ [3a,5]. This last is less hindered but also less basic than L–L, so that its coordinating behaviour is expected to be at least as different as it was found to be when coordinated to zinc, cadmium [3b], or mercury(II) [3c].

An additional reason for investigating the title compounds lies in the report that (although some organotin(IV) compounds are toxic) some of their derivatives containing bidentate nitrogen ligands, such as 2,2'-bipyridyl or *ortho*-phenanthro-

line, show antitumour activity [6]; in pursuance of this line of research, other adducts of organotin(IV) species with diamines have been described and characterized, mainly in the solid state with the help of infrared and Mössbauer spectra (for example, adducts with 1,2-ethylenediamine or with 1,4-butanediamine [7a]), although in these instances the resulting compounds were found to be too toxic to be useful as anticancer agents [7b].

Results and discussion

Solid, air-stable adducts were obtained as precipitates by treatment of the $R_{4-n}SnX_n$ compounds with the ligands in petroleum ether or, in the case of $SnBr_4$ and SnI_4 , in a mixture of petroleum ether and diethyl ether. As previously found [3a] for bis(pyrazol-1-yl)methane, no compound was obtained by interaction of $R_{4-n}SnX_n$ ($R = \text{methyl or phenyl}$; $X = \text{Cl, Br}$) and the ligand $L-L$ or $L'-L'$ when $n = 0$ or $n = 1$, in agreement with the very low acidity of these organotin(IV) species. The compounds obtained are listed in Table 1, and spectral data are in Tables 2, 3, 4 and 5; they are air- and moisture-stable, and are often insoluble in chloroform or

Table 1
Some physical data for the compounds prepared

Compound	M.p. (°C)	Yield (%)	Elemental analyses (%) ^a			Specific conductivity ^b (ohm ⁻¹ cm ² mol ⁻¹)
			C	H	N	
I (L-L)SnCl ₄ ^c	237-239	88	28.26 (28.43)	3.57 (3.47)	11.76 (12.05)	(0.96) 53.3
II (L-L)SnBr ₃ OH ^c	161-163	71	22.36 (22.79)	3.04 (2.96)	9.45 (9.67)	(1.03) 67.4 (1.01) 343.6 *
III (L-L)SnI ₄	122-124	46	15.94 (15.91)	2.17 (1.94)	6.33 (6.75)	(1.00) 170.3
IV (L-L)MeSnCl ₃	178-180	61	32.62 (32.44)	4.24 (4.31)	12.62 (12.61)	(0.96) 137.4
Va (L-L) ₃ (Me ₂ SnCl ₂) ₂	134-136	58	42.45 (42.24)	5.61 (5.75)	15.95 (15.97)	(1.10) 35.75
Vb (L-L)Me ₂ SnCl ₂	84- 86	62	36.65 (36.83)	5.43 (5.23)	13.34 (13.22)	(1.13) 28.32
VI (L-L)C ₆ H ₅ SnCl ₃	194-196	96	40.46 (40.32)	4.25 (4.18)	10.84 (11.06)	(0.99) 84.7
VII (L-L)(C ₆ H ₅) ₂ SnCl ₂	165-167	81	50.12 (50.40)	4.75 (4.78)	10.30 (10.22)	(1.00) 7.7 (1.00) 48.0 *
VIII (L'-L')SnCl ₄ ·1H ₂ O	280 dec.	87	23.53 (23.77)	2.85 (3.10)	12.50 (12.32)	(0.99) 70.1
IX (L'-L')MeSnCl ₃	300 dec.	75	28.60 (28.85)	3.68 (3.63)	13.70 (12.46)	(1.06) 161.3
X (L-L')C ₆ H ₅ SnCl ₃	192-193	84	37.42 (37.66)	3.63 (3.58)	11.82 (11.71)	(1.03) 57.3

^a Calculated values in parentheses. ^b Acetone solution at room temperature and at the molar concentration $\times 10^{-3}$ indicated in parentheses. The solvent was methanol for the starred data (*). ^c Additional data: Compound I Cl: 30.08 (30.51)%; Compound II Br: 41.82 (41.35)%; O: 2.34 (2.76)%; Compound VIII Cl: 30.71 (31.19)%.

Table 2

Selected infrared data (Nujol mull) cm^{-1}

Compound	(C-H) azole	1500-1600	< 500	others
L-L	3140w 3100w	1565sh 1560sh	475s 405w 360w 310m 280m	
I	3150w 3120m 3040w	1565s 1560sh	475w 430vw 390m 310m 280w	330s SnCl
II	3140w 3120m	1585m 1560m	475vw 310vw	3350br (OH) 2600br
III	3130w 3100w	1580s, sh 1565s	470w 330w	
IV	3140w	1570s	380w 290w	330w SnCl
Va	3140w	1580m 1565m	480vw 465w 390vw	
Vb	3140w	1580m 1560m	480vw 465w 360w	320w SnCl
VI	3140w	1560s	495vw 485w 460m 370w 290m	340sh SnCl 330w SnCl
VII	3140w	1580w 1560s	490m 480m 470s 460s, sh 380w 290s, sh 275s	330w SnCl
L'-L'	3135m 3110m	1520m 1510sh	395s 360m	
VIII	3160m 3140s	1510m	380m 285w 260w	340s, br SnCl 3340w (H_2O)
IX	3170w 3140sh 3130w 3100w	1510m	385w 370w 280s	320m SnCl
X	3180sh 3160w 3140w 3130w	1510w	460s 380m 290s 260m	320m SnCl

dichloromethane, soluble in acetone, and sometimes in methanol, but insoluble in water. Their compositions were confirmed by the analytical data which are listed in Table 1 together with melting points, and specific conductivities.

Table 3
Proton NMR data

Compound	Solvent (a)	CH ₂ , singlet	4-CH, singlet	3- and 5-Me, singlet	R-Sn and notes
CH ₂ (3,5-Me ₂ pz) ₂	L-L chloroform	6.04	5.78	2.41, 2.18	^b
CH ₂ (3,5-Me ₂ pz) ₂	L-L acetone	6.03	5.75	2.44, 2.06	
CH ₂ (3,5-Me ₂ pz) ₂	L-L methanol	6.02	5.82	2.38, 2.12	
(L-L)SnCl ₄	acetone, r.t.	7.06 ^c	6.46 ^c	2.84, 2.69	^{d,e}
(L-L)SnCl ₄	acetone, -20°C	7.33 ^c	6.36, 6.15 ^c	2.59, 2.27	^{f,e}
(L-L)SnBr ₃ (OH)	I	6.47	6.40 ^g	2.81, 2.70	^{d,h}
(L-L)SnBr ₃ (OH)	II	6.47	6.14 ^g	2.58, 2.25	^{f,h}
(L-L)SnI ₄	acetone	6.28	5.95	2.47, 2.12	ⁱ
(L-L)SnI ₄	methanol	6.30	6.14	2.47, 2.25	ⁱ
(L-L)MeSnCl ₃	acetone	6.56	6.26	2.60, 2.30	
(L-L) ₃ (Me ₂ SnCl ₂) ₂	acetone	6.57	6.23	2.60, 2.38	Me: 1.42s, J ca. 116
(L-L) ₃ (Me ₂ SnCl ₂) ₂	acetone	6.14	5.83	2.47, 2.10	Me: 1.23s, J 81, 87
(L-L) ₃ (Me ₂ SnCl ₂) ₂	methanol	6.32	6.16	2.48, 2.27	Me: 1.12s, J 87, 90
(L-L)Me ₂ SnCl ₂	chloroform	6.18	5.85	2.21, 2.48	Me: 1.25s, J 84, 88
(L-L)PhSnCl ₃	acetone	6.50	6.07	2.52, 2.20	Ph: 7.2-8.0m; ^{d,j}
(L-L)Ph ₂ SnCl ₂	methanol	6.53	6.31	2.82, 2.63	Ph: 7.2-8.0m; ^{f,j}
(L-L)Ph ₂ SnCl ₂	methanol	6.07	5.88	2.38, 2.14	Ph: 7.3-8.0m

	C(Me) ₂ singlet	4-CH (<i>J</i> ca. 2 Hz, if triplet)	3- and 5-CH (<i>J</i> ca. 1 or 2 Hz, if doublet)
Me ₂ C(pz) ₂	2.24	6.23t	7.55d, 7.46d
Me ₂ C(pz) ₂	2.24	6.30t	7.58d, 7.48d
Me ₂ C(pz) ₂	2.28	6.27t	7.58d, 7.42d
Me ₂ C(pz) ₂	2.23	6.20t	7.52d, 7.23d
(L'-L')SnCl ₄ ·H ₂ O	2.30, 2.33 ^k	6.70-6.80m	8.1-8.4m
(L'-L')SnCl ₄ ·H ₂ O	2.30, 2.33 ^k	6.90-7.05m	8.4-8.8m
(L'-L')MeSnCl ₃	2.31	6.71t ^d , 6.54s,	8.20d ^d , 7.59d,
		6.25t	7.50br
(L'-L')MeSnCl ₃	2.31	7.53t ^d , 6.58s,	8.25d ^d , 7.61d,
		6.28t	7.50d
(L'-L')MeSnCl ₃	2.31	6.68br ^d , ca.	8.48br ^d , 7.78d,
		6.5, 6.33t	7.57d
(L'-L')PhSnCl ₃	2.30	6.34t ^d , 6.64t	7.4-8.3 ⁿ
(L'-L')PhSnCl ₃	2.23	6.33t ^d , 6.63t	7.0-8.1 ⁿ

^a Deuterated solvent at room temperature unless not stated otherwise. ^b From ref. 11. ^c Methylene and 4-CH signal could possibly be interchanged. ^d Isomer A, the more abundant. ^e A/B ca. 1.4. ^f Isomer B, the less abundant. ^g These assignments could possibly be interchanged. ^h A/B ca. 1. ⁱ No HO signal detected. ^j A/B ca. 5. ^k Region obscured by the solvent. ^l A/B ca. 2. ^m A/B ca. 3. ⁿ Phenyl, 3-CH and 5-CH protons overlap.

Table 4

Carbon NMR data

Compound	Solvent ^a	C-3	C-4	C-5	CH ₂	Methyl	
CH ₂ (3,5-Me ₂ pz) ₂	L-L	chloroform	148.3	106.4	140.5	60.5	13.5, 11.2
CH ₂ (3,5-Me ₂ pz) ₂	L-L	acetone	147.7	105.8	140.3	59.5	13.0, 10.5
CH ₂ (3,5-Me ₂ pz) ₂	L-L	methanol	149.9	107.3	142.3	60.6	13.3, 11.1
CH ₂ (3,5-Me ₂ pz) ₂	L-L	DMSO	147.1	105.6	140.0	58.9	13.3, 10.8
(L-L)SnCl ₄	I	acetone ^b	153.4	109.2	143.8	59.3	150, 12.3, 10.7
			148.7	107.2	143.0	55.1	
(L-L)SnBr ₃ (OH)	II	methanol	150.3	108.4	144.6	60.0	12.6, 11.1
(L-L)SnI ₄	III	acetone	149.1	108.0	144.3	59.1	12.0, 10.7
(L-L)MeSnCl ₃	IV	acetone	148.7	106.9	141.9	58.9	21.3 ^c , 12.7, 10.5
(L-L) ₃ (Me ₂ SnCl ₃) ₂	Va	chloroform	148.3	107.7	144.0	58.9	14.0, 12.3, 11.5
(L-L) ₃ (Me ₂ SnCl ₃) ₂	Va	methanol	150.3	108.6	145.2	59.8	14.1, 12.4, 11.1
(L-L) ₃ (Me ₂ SnCl ₃) ₂	Va	DMSO	147.1	105.8	140.4	58.8	24.1, 13.2, 10.8
(L-L)Me ₂ SnCl ₂	Vb	chloroform	148.2	106.8	140.4	60.1	14.0, 12.1, 11.0
(L-L)PhSnCl ₃	VI	acetone ^h	^h	109.2	^h	58.8	12.6, 10.6
			^h	107.1	^h	^h	^h
(L-L)Ph ₂ SnCl ₂	VII	methanol ^d	^d	107.4	^d	60.6	12.8, 10.6
							Others and notes
Me ₂ C(pz) ₂	L'-L'	acetone	140.9	107.5	129.0	^e	
Me ₂ C(pz) ₂	L'-L'	methanol	140.8	106.9	128.9	^e	
(L'-L')SnCl ₄ ·H ₂ O	VIII	acetone	139.1	106.7	133.0	^e	
			138.8	104.2	132.6		
(L'-L')MeSnCl ₃	IX	acetone	^f	105.9	134.6	^{e,g}	
				106.9			
(L'-L')PhSnCl ₃	X	acetone	141.0	105.9	133.5	^e ; Ph: 128.1, 129.3, 131.0	
				106.9			

^a Deuterated solvents at room temperature. ^b There are two isomers in ca. 1/1 ratio, and so the signals belonging to each isomer cannot be assigned. ^c The signal at 21.3 is doubtful. ^d C-3 and C-5 are not observed. Additional signals at 129.5, 131.2 and 136.2 due to the phenyl group. ^e The quaternary carbon was not observed; the signals due to the geminal methyl group overlap with those of acetone. ^f Not observed. ^g Me-Sn not observed. ^h There are two isomers, the more abundant characterized by the signals listed in the upper line. Some signals cannot be detected.

While the unsubstituted donor, (Pz)₂CH₂, was found [3a] to react with all R_{4-n}SnCl_n acceptors where n = 4, 3, or 2 and R is either methyl or phenyl as well as with Ph_{4-n}SnBr_n (n = 2 or 4), a different pattern of reactivity is present here. Thus, both (Me₂pz)₂CH₂ and excess (Pz)₂CMe₂ (1/2) reacted with anhydrous tin(IV) chloride and with either methyl- or phenyl-trichlorotin, but only the former (more basic) ligand gave an adduct with either diphenyl- or dimethyl-dichlorotin. In addition, the adduct, II, of L-L with tin(IV) bromide, was found to contain one OH group in the place of a bromide, probably because of the presence of traces of moisture and one of the adducts with L'-L' was found to be the hydrated compound VIII, (L'-L')SnCl₄·H₂O; no interference by water was observed when bis(pyrazolyl)methane was employed [3a]. Treatment of L-L with dimethyldichlorotin under our conditions gave compound Va as a deep-yellow 3/2 adduct, while when a 1/1 ratio was used, either at room temperature or [5] in boiling hexane, a colourless 1/1 adduct Vb is obtained, and has a different melting point. The formula Va suggests either a seven-coordinated, (L-L)-bridged coordination on the

Table 5

Tin NMR data

Compound ^a		Signals (ppm) from tetramethyltin(IV) (relative intensities (%))
SnCl ₄		-18.9
(L-L)SnCl ₄	I	-110
(L-L)MeSnCl ₃	IV	-287 (15 ppm broad)
MeSnCl ₃		-150
Me ₃ SnCl		-110.4
(L-L)PhSnCl ₃	VI	-182, -76, -38, +94 (54, 16, 8, 22%, respectively)
(L-L)Ph ₂ SnCl ₂ *	VII	-223, -168, -105, +37 (ca. 10, 10, 10, 70% respectively)
Ph ₂ SnCl ₂ *		-227.2
(L'-L')SnCl ₄ · H ₂ O	VIII	-104.8, -95.7, -91.6, -38.2, -37.4, -23.4 (9, 42, 9, 13, 11, 16% respectively)
(L'-L')PhSnCl ₃	X	-108, -25, +100 (ca. 15, 15, 70% respectively)
PhSnCl ₃		-256.9

^a Perdeuterioacetone solvent for all the compounds, except those marked *; since these are insoluble in acetone CD₃OD was used. Both (L-L)SnBr₃(OH), II, and (L-L)SnI₄, III, were not sufficiently soluble.

tin(IV) atom or, more simply, the presence of a clathrated molecule, as previously found in [(Pz)₂CH₂]PhSnCl₃ · $\frac{1}{4}$ Et₂O [3a] or in both of the crystalline forms of *cis*-dichlorobis(4-chlorophenyl)(4,4'-dimethyl-2,2'-bipyridyl) · *n*toluene, where *n* = 1 or 1.5 [8].

The infrared data (Table 2) show all the bands required for the presence of the donor and of the acceptor; an OH stretching vibration was found in II and VIII and an Sn-Cl vibration in IV, VI, VII, VIII, IX and X, respectively. Although from the position of the C-Sn, Cl-Sn and N-Sn bands it is sometimes possible to draw conclusions about the arrangement of the ligands around the tin atom [7a] we did not attempt such an assignment, there are several bands in the low frequency region, and any conclusion, valid only for the solid state, should be supported by Mössbauer spectra (or, better, by single crystal X-ray structure determinations), which not available to us.

The electrical conductivities were measured for all the compounds listed in acetone solution in which the typical 1/1 electrolyte tetra-*n*-butylammonium bromide has a specific conductivity of 137 ohm⁻¹ cm² mol⁻¹. Some of them are non-electrolytes (V and VII) other electrolytes (III, IV and IX), and the remaining compounds are at least partly ionized. Two different types of ionic dissociation are in principle possible for all the compounds under consideration except for V and VII, in the case of compound I they can be represented as follows (solvent = acetone or water; *n* = 0 or 1)

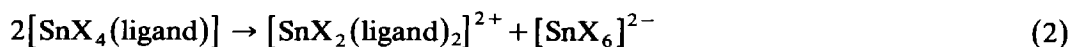
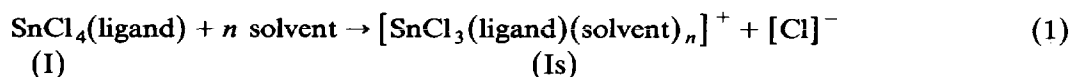


Table 6

Molecular weight determinations ^a

Compound	Formula weight (FW)	Solvent	conc. (% w/w)	MW	MW/FW
I	467.8	Acetone	2.61	302 ^b	0.65
			1.25	280 ^c	0.60
II	579.7	Acetone	1.07	322	0.55
		Methanol	1.30	unstable	
III	830.6	Acetone	1.00	unstable	
IV	444.4	Acetone	1.24	222	0.50
Va	1052.2	Chloroform	1.20	266 ^b	0.25
			0.44	231 ^b	0.22
			1.01	293 ^c	0.28
VI	506.5	Acetone	1.07	236	0.47
VII	548.1	Acetone	1.77	388	0.71
VIII	454.7	Acetone	1.03	232	0.51
IX	416.3	Acetone	1.07	178	0.43
X	478.4	Acetone	0.95	235	0.49

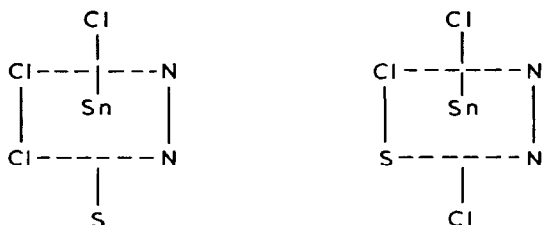
^a By osmometry. ^b Determination with thermistor probes for non-conducting solutions. ^c Determination with special isolated thermistor probes.

The latter type of dissociation is ruled out by the observation that the molecular weight found by osmometry in acetone is always much smaller than the formula weight (Table 6). For the two compounds which are nm-electrolytes, [(Me₂pz)₂CH₂]₃(Me₂SnCl₂)₂, (Va) and [(Me₂pz)₂CH₂][Ph₂SnCl₂] (VII), the low value of the molecular weight found shows that in chloroform or acetone they undergo extensive dissociation into the starting reagents. This same type of dissociation, this time practically complete, accounts for the fact that no adduct could be obtained from these two organotin acceptors and the less basic (Pz)₂CH₂ ligand.

The proton (Table 3) and carbon NMR (Table 4) spectra gave additional support to the proposed formulae, showing that no rearrangement of the organic ligand has taken place upon reaction. In agreement with our previous experience with zinc, cadmium [3b,2a], or mercury(II) derivatives [3c,2b] of these or related ligands, the ¹H chemical shifts of the L-L or L'-L' protons are generally displaced to lower field upon coordination, while in the ¹³C spectra the ring carbons move downfield upon coordination but the CH₂ carbon moves upfield. In two cases, [(Me₂pz)₂CH₂]₃(Me₂SnCl₂)₂ (Va) and (Pz)₂CMe₂ · Me₂SnCl₂ (VII), the displacement upon coordination is very small (i.e. not more than 0.11 ppm), in agreement with extensive dissociation and exchange in solution. The presence of only one signal for the CH₂ or the CMe₂ protons (or for the corresponding carbon atoms) in most of the derivatives of (Me₂pz)₂CH₂ or of (Pz)₂CMe₂ (II, III, IV, V, VII, or IX and X, respectively) shows that the boat-shaped six-membered Sn(N-N)₂C cycle is not rigid, so that rapid inversion makes the relevant nuclei magnetically equivalent. In the remaining compounds (I, VI, or VIII), two CH₂, or CMe₂, signals are present but are not always in the 1/1 ratio required if the Sn(N-N)₂C cycle were rigid; at the same time, in these compounds, as well as in IX or X, more than one set of signals is observed for the pyrazole ring protons (or for the corresponding carbon atoms); since the intensity ratio between the sets is often different from unity, the

presence of more than one species in solution must be assumed, in keeping with another line of evidence. In several ^{119}Sn spectra, those of VI, VIII, or IX (Table 5), more than one signal is observed, namely four for VI, several for VIII, and three for X. In all the cases investigated (Table 5), none of the signals observed in acetone solution corresponds to that observed for the corresponding Lewis acid in the same solvent, thus providing additional evidence against dissociation into the starting reagents. However, such a dissociation appears to occur in the case of $\text{Ph}_2\text{SnCl}_2(\text{L-L})$, VII, as shown by the presence of a signal at -223 ppm, very near to that found at -227 ppm for Ph_2SnCl_2 in the same solvent; this type of dissociation is favoured also by the molecular weight determination mentioned above.

The presence of isomers may appear surprising for some of the adducts reported here. For example, in the most simple of all our compounds, $[(\text{Me}_2\text{pz})_2\text{CH}_2]\text{SnCl}_4$ (I) a pseudo-octahedral solid-state structure is likely, for which no isomer is possible, even if the $\text{Sn}(\text{N-N})_2\text{C}$ moiety were rigid. Nevertheless, in solution two sets of ^{13}C or ^1H NMR signals are observed, both in the proton and in the carbon NMR spectrum, and they are accounted for in terms of the presence of an equilibrium of type (a) above: one set corresponds to the unsolvated molecule I and the other to the solvated cation, for which, if $n = 1$, a facial and a meridional isomer are possible:



Although in the case of I no additional support is provided by the ^{119}Sn spectrum, where only one signal is observed owing to a rapid interconversion of the different species, in the other adduct of tin tetrachloride, $[\text{Me}_2\text{C}(\text{pz})_2]\text{SnCl}_4 \cdot \text{H}_2\text{O}$ (VIII), several species can be detected in acetone solution, in which the solute is mainly ionized; here, in addition, two sets of signals are clearly seen in the ^{13}C NMR spectrum, and two sets are also compatible with the proton NMR spectrum. No assignment of the signals observed in the ^{119}Sn spectrum were attempted because there are not enough suitable reference data available, and because the pairwise-additivity model appears not to be applicable to complexes containing different ligands in addition to halides [9]; furthermore, the quality of the spectra is sometime only fair owing to the poor solubility of some of our compounds, so that some additional signal might go undetected.

Similar considerations can be extended to the other species which were found to be electrolytes in the solvent used for the NMR spectra, so that both ionized and un-ionized species are likely to be present, and a number of isomers is possible. By comparison, geometrical isomers were detected [10], e.g. by ^{19}F NMR spectroscopy for mixed fluorostannates(IV) [10b] and by ^{119}Sn NMR spectroscopy for mixed pseudohalogenostannates(IV) [10c]; in addition, *cis*- and *trans*-derivatives were recently identified by X-ray single crystal structure determinations carried out on the adducts of dichlorobis(4-chlorophenyl)tin with 4,4'-dimethyl-2,2'-bipyridyl [8].

Observation of isomers stable in solution is possible probably because most of the compounds we have studied here are ionized in polar solvents, so that in the resulting cation the acid tin(IV) site becomes more acceptor than in un-ionized tin(IV) derivatives, such as those of bis(pyrazol-1-yl)methane reported previously [3a]. The presence of isomers is evident only in the compounds formed from the most acid acceptors, i.e.: I or VIII (from tin tetrachloride), VI or IX (from R_3Sn); they have not been found for the derivatives of the least acid acceptors, e.g. V (from Me_2SnCl_2) or VII (from Ph_2SnCl_2), which in solution dissociate into the starting reagents.

The combined evidence from measurements carried out in solution (molecular weight determinations, conductivity, proton, carbon, and tin NMR spectra) gives here a picture which is quite different from that obtained for tin(IV) derivatives of $(Pz)_2CH_2$. Clearly a fine balance between electronic and steric effects operates to determine the behaviour in solution of tin(IV) and of organotin(IV) adducts of bis(pyrazolyl)methane and of its simple derivatives we have employed. In spite of the more marked Lewis-acid character of tin(IV) than of the corresponding zinc, cadmium or mercury(II) acceptors, this balance is more sensitive in the case of the adducts of bis(pyrazolyl)methanes with the tin cation than with those of the other elements, probably because the coordination numbers reached are generally lower with the group IIB derivatives. Consequently, generalizations about pharmaceutical (or any other) property of this or of a related class of adducts of $R_{4-n}SnX_n$ should be made with extreme caution, since it is evident that small variations of any of the constituent parts may give rise to different behaviour in solution, where, apart from possible dissociation into the starting reagents, un-ionized and ionized forms may coexist, and geometric isomers are possible.

Experimental

The samples were dried in vacuo to constant weight (20 °C, ca. 0.1 torr). Carbon, hydrogen, and nitrogen analyses were carried out in this Department. The molecular weight determinations were performed by the Pascher's Mikroanalytisches Laboratorium, Remagen, F.R.G. Infrared spectra from 4000 to 250 cm^{-1} were recorded on a Perkin-Elmer 457 instrument. 1H , ^{13}C and ^{119}Sn NMR spectra were recorded on Varian EM-390, FT80A and VX-300 spectrometers operating at room temperature (90, 20 and 111.9 MHz). The electrical resistance of solutions was measured with a Philips GM-4249 bridge at room temperature. Melting points were measured with a IA 8100 Electrothermal Instrument.

[Bis(3,5-dimethylpyrazol-1-yl)methane]tetrachlorotin(IV) (I)

Anhydrous $SnCl_4$ (2.0 mmol), was added to a stirred petroleum ether solution (40 ml) of the ligand bis(3,5-dimethylpyrazol-1-yl)methane 0.82 g. (40 ml, 4 mmol). After evaporation of the solution to dryness under reduced pressure, the glassy residue was stirred with diethyl ether (20 ml). The white product obtained was filtered off and washed with petroleum ether and diethyl ether. The adduct VIII was obtained similarly.

[Bis(3,5-dimethylpyrazol-1-yl)methane]tetraiodotin(IV) (III)

A diethyl ether solution (25 ml) of SnI_4 (627 mg; 1.0 mmol) was added to a stirred diethyl ether solution (25 ml) of the ligand bis(3,5-dimethylpyrazol-1-

yl)methane (420 mg; 2.05 mmol). A brown precipitate, III, was obtained immediately; it was filtered off, and washed with diethyl ether. Compound II (yellow) was obtained similarly.

[2,2'-Bis(pyrazol-1-yl)propane]methyltrichlorotin(IV) (IX)

To a stirred petroleum ether solution (25 ml) of CH_3SnCl_3 (480 mg, 2 mmol) at room temperature was added a petroleum ether solution (25 ml) of [2,2'-bis(pyrazol-1-yl)propane] (712 mg, 4.04 mmol). A white precipitate was formed immediately, and this was filtered off, washed with petroleum ether and diethyl ether and shown to be X. Adducts IV (white), V (yellow), VI (pale yellow), VII and X (white) were obtained similarly.

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