SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF TIN(IV) AND ORGANOTIN(IV) DERIVATIVES OF BIS(AZOL-1-YL)METHANES

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Abstract

A series of 1:1 adducts of the type $[(L)R_nSnX_{4-n}]\cdot yH_2O$ (L = bis(imidazol-1-yl)methane ($\mathbf{L^I}$) or bis(1,2,4-triazol-1-il)methane ($\mathbf{L^T}$); R = Me, Et, Bu^n or Ph; X = I, Br or Cl; n = 0, 1, 2 or 3; y = 0, 1, 1.5 or 2) have been synthesized and characterized in the solid state and in solution by analyses, spectral (IR, far-IR, ^1H and ^{119}Sn NMR) data and conductivity measurements. Some of them are likely polymeric in the solid state. The tri- and di-organotin(IV) compounds generally dissociate in DMSO solution, while the tri- and tetrahalide adducts partially retain the hexacoordinate configuration.

Introduction

Coordination compounds of tin(IV) and organotin(IV) halides with nitrogen-donor ligands have been extensively synthesized and described(1). Interest in such systems arises because of their structural features(2) and biological relevance(3): for example some organometallic tin(IV) compounds are known to be toxic, whereas some others are found to be active against P388 leukaemia(4).

We have recently reported analytical, structural and spectroscopic data pertinent to tin(IV) and organotin(IV) complexation with bidentate poly(azol-1-yl)alkanes(2,5,6), a family of stable and flexible bidentate ligands.

It has been shown(2,5,6) that this class of donors is able to form stable 1:1, 2:1, 3:2, and 2:3 acid-base adducts and also hydrolysis products. In some cases they can also undergo cleavage of the $C(sp^3)$ bridging-N bond(2).

So, it seemed pertinent to extend this investigation to the study of the interaction between several R_nSnX_{4-n} acceptors and the new donors bis(imidazol-1-yl)methane ($\mathbf{L^I}$) and bis(1,2,4-triazol-1-yl)methane ($\mathbf{L^T}$) (Fig.1).

These ligands are more basic(7) with respect to the others previously investigated and are also able to form stable polynuclear derivatives(8).

The synthesis, analytical and spectroscopic (IR, far-IR, ^1H and ^{119}Sn NMR) characterization of 21 new tin(IV) and organotin(IV) complexes are reported in this paper.

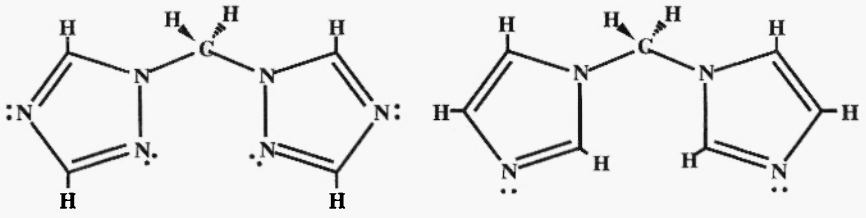

Fig. 1. The donors $\mathbf{L^I}$ and $\mathbf{L^T}$

Materials and Methods

The tin(IV) and organotin(IV) halides were purchased from Alfa and Aldrich, and used as received. The samples for microanalysis were dried in vacuo to constant weight (20°C, ca. 0.1 Torr). Elemental analyses (C,H,N) were perfomed in house with a Carlo-Erba model 1106 instrument. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^1H and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^1H and 111.9 MHz for ^{119}Sn). Melting points were taken on an IA 8100 Electrothermal instrument. The electrical conductance of the solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

Synthesis of the ligands

The ligand bis(1,2,4-triazol-1-yl)methane (**L^T**) and bis(imidazol-1-yl)methane (**L^I**) were prepared according to the literature method(9).

Synthesis of the complexes

[{Bis(imidazol-1-yl)methane}trimethylchlorotin(IV)] **1**
To a stirred diethyl ether solution (25 ml) of $(CH_3)_3SnCl$ (800 mg, 4.0 mmol) at room temperature was added an ethanol solution (25 ml) of bis(imidazol-1-yl)methane, **L^I**, (452 mg, 3.0 mmol). A colourless precipitate was formed immediately, and was filtered off, washed with diethyl ether and shown to be compound **1**.

[{Bis(imidazol-1-yl)methane}dimethyldichlorotin(IV)] **2**
To a stirred ethanol solution (25 ml) of $(CH_3)_2SnCl_2$ (440 mg, 2.0 mmol) at room temperature was added an ethanol solution (25 ml) of bis(imidazol-1-yl)methane, **L^I**, (604 mg, 4.0 mmol). A colourless precipitate was formed immediately, and was filtered off, washed with ethanol/diethyl ether and shown to be compound **2**. Adducts **3-13** and **15-20**, were obtained similarly.

[{Bis(imidazol-1-yl)methane}dimethyl$(H_2O)_2$tin(IV)]$(BF_4)_2$ **14**
An ethanol suspension (100 ml) of compound **2** (730 mg, 2.0 mmol) was introduced into a 250-ml round-bottomed flask fitted with a condenser. Silver tetrafluoroborate (590 mg, 3.0 mmol) was then added. The mixture was heated at reflux, under N_2 stream, with stirring for 1 day. It was then allowed to cool and filtered off. The solvent was removed with a rotary evaporator and the residue was extracted with CH_2Cl_2 (3 x 15 ml); the organic layer was dried on Na_2SO_4. It was then filtered and concentrated under reduce pressure. Et_2O (30 ml) was then added. A colorless precipitate was formed which was filtered off, washed with diethyl ether and shown to be compound **14**.

[Bis(1,2,4triazol-1-yl)ethane]tetrachlorotin(IV)·(H_2O) **21**
Anhydrous $SnCl_4$ (521 mg, 2.0 mmol) was added to a stirred acetone solution (50 ml) of the ligand **L^T** (304 mg, 2.0 mmol), under a stream of N_2. A colourless precipitate was obtained immediately; it was filtered off and washed with Acetone/Et_2O under a stream of N_2 and shown to be compound **21**.

Results and Discussion

The interaction between **L^I** or **L^T** (**L** in general) and tin(IV) and organotin(IV) compounds was generally carried out in ethanol or in acetone and gave the adducts **1-13** and **15-21**, listed in Table **1**, with exception of the derivative **1**, which was synthesized in diethyl ether in the presence of a strong excess of the triorganotin acceptor (eq. *1*).

$$L + R_nSnX_{4-n}\cdot yH_2O \longrightarrow [(L)R_nSnX_{4-n}]\cdot yH_2O \qquad (1)$$

1-13, 15-21

With the donor **L^T**, which is less basic with respect to **L^I**, no derivatives could be isolated under our conditions when trimethyl- or triphenyl tin(IV) chloride was employed, but not even with dichloro- or dibromodi-n-butyltin(IV). The reactions of $\mathbf{L^I}$ and $\mathbf{L^T}$ with dimethyltin(IV) fluoride and tin(IV) fluoride were equally unsuccessfull. The metathesis of chloride by tetrafluoroborate groups in the complex **1**, leads to the formation of the complex **14**, in accordance with eq. *2*.

$$[(L^I)(CH_3)_2SnCl_2] + 2\,AgBF_4 \longrightarrow \underset{\mathbf{14}}{[(L^I)(CH_3)_2Sn(H_2O)_2](BF_4)_2} + 2AgCl \qquad (2)$$

All the compounds obtained are solid. They are colourless with exception of **13** which is blood red, colour resulting from what is known as an electronic charge-transfer absorption (typical of many halide compounds).

All the derivatives of $\mathbf{L^I}$ were substantially insoluble in water, benzene, acetonitrile, ethanol, methanol and chlorinated solvents, poorly soluble in hot acetone and moderately soluble in DMSO.

The derivatives of $\mathbf{L^T}$ were more soluble with respect to those of $\mathbf{L^I}$. The poor solubility of most of the adducts of $\mathbf{L^I}$, suggests the formation of polymeric or oligomeric structure as those shown in Fig.2.

Various amounts of water from 1 in $\mathbf{[(L^I)CH_3SnCl_3]\cdot H_2O}$ (**1**), to 1.5 in $\mathbf{[(L^I)SnBr_4]\cdot 1.5(H_2O)}$ (**12**) and finally to 2 in $\mathbf{[(L^T)C_6H_5SnCl_3]\cdot 2H_2O}$ (**20**) are probably due to traces of moisture in the starting reagents.

If the complex $\mathbf{[(L^T)(CH_3)_2SnCl_2]}$ (**15**) is treated with mercuric or ferrous chloride, the mercuric or ferrous complex of bis(1,2,4-triazol-1-yl)methane ($\mathbf{L^TMCl_2}$; M = Hg or Fe) was immediately precipitated, whereas the reaction between $\mathbf{[(L^T)C_4H_9SnCl_3]}$ **19** and $HgCl_2$ was always unsuccessfull.

The conductivity measurements were carried out for all the compounds in DMSO. In this solvent, the derivative **1** is non electrolyte; compounds **2**, **5**, **7**, **9**, **11**, **15**, **18**, **19** and **20** are partly ionized, whereas all the other tin(IV) adducts are 1:1 (**3**, **4**, **6**, **8**, **10**, **16** and **17**) or 2:1 electrolytes (**12**, **13** and **21**), in accordance with the following equations *3-6*:

$$[(L)R_nSnX_{4-n}]\cdot yH_2O + x(DMSO) \rightleftharpoons [(L)R_nSnX_{4-n-1}(DMSO)_x]^+ + [X]^- + yH_2O \qquad (3)$$

$$[(L)R_nSnX_{4-n}]\cdot yH_2O + x(DMSO) \rightleftharpoons [R_nSnX_{4-n-1}(DMSO)_x]^{++} + [X]^- + L + yH_2O \qquad (4)$$

$$[(L)R_nSnX_{4-n}]\cdot yH_2O + x(DMSO) \rightleftharpoons [(L)R_nSnX_{4-n-2}(DMSO)_x]^{++} + 2[X]^- + yH_2O \qquad (5)$$

$$[(L)R_nSnX_{4-n}]\cdot yH_2O + x(DMSO) \rightleftharpoons [R_nSnX_{4-n-2}(DMSO)_x]^{++} + 2[X]^- + L + yH_2O \qquad (6)$$

We also found that the conductance of the tin(IV) complexes is strongly dependent from the concentration: for example the values of the specific conductivity of adducts **19** and **20** are higher in a more dilute solution.

It was not possible to perform molecular weight determinations due to poor solubility of the complexes.

IR data

The relevant IR data of the donor $\mathbf{L^I}$ and of its derivatives **1-14** are reported in Table 2 whereas those of $\mathbf{L^T}$ and of its derivatives **15-21** are reported in Table 3. All the spectra shows weak vibrations at ca. 3000 cm^{-1} due to C-H stretching of the heterocyclic ring and others more intense between 1600 and 1500 cm^{-1}, typical of ring breathing(10).

The tetrafluoborato group in the adduct **14** was found to be ionic, a single broad absorption at ca. 1100 cm^{-1} and a sharp band at 620 cm^{-1} being observed(11). This compound show also a broad band at ca. 390 cm^{-1} likely due to ν(Sn-O) absorption. On this basis we suggest the water may be coordinated to tin(IV) acceptor.

In the far IR region, the spectra of complexes **1-21** correspond closely to those of other bis(azol-1-yl)alkane tin(IV) derivatives(2,5,6). On this basis we assigned the strong bands at ca. 570 cm^{-1} in dimethyltin(IV) derivatives **2**, **3**, **15** and **16** to ν_{asym} Sn-C. Only a single Sn-C band appeared also in the spectra of di-n-butyl and diethyltin(IV)derivatives in accordance with a trans-octahedral configuration of the two alkyl groups(12).

Table 1
Physical, Analytical and Conductivity Data of Derivatives **1**-**21**.

Compound and formula	No	Yield %	m.p. °C	Elemental analysis C	H	N	Λ	conc.[a]
$[(L^I)(CH_3)_3SnCl]\cdot H_2O$ $C_{10}H_{19}ClN_4OSn$	**1**	70	65dec	32.7 32.9	5.2 5.2	15.5 15.3	3.0	1.0
$[(L^I)(CH_3)_2SnCl_2]$ $C_9H_{14}Cl_2N_4Sn$	**2**	90	238dec	29.7 29.4	3.5 3.8	15.3 15.2	17.5	1.0
$[(L^I)(CH_3)_2SnBr_2]$ $C_9H_{14}Br_2N_4Sn$	**3**	95	228-230	23.3 23.7	3.2 3.1	11.8 12.3	33.2	1.1
$[(L^I)(C_2H_5)_2SnBr_2]$ $C_{11}H_{18}Br_2N_4Sn$	**4**	89	256-258	27.0 26.9	3.9 3.7	11.4 11.6	41.4	0.3
$[(L^I)(C_4H_9)_2SnCl_2]$ $C_{15}H_{26}Cl_2N_4Sn$	**5**	50	180-182	39.7 39.9	6.1 5.8	12.3 12.4	21.7	0.3
$[(L^I)(C_4H_9)_2SnBr_2]$ $C_{15}H_{26}Br_2N_4Sn$	**6**	93	193-194	33.5 33.3	5.1 4.9	10.4 10.4	35.5	1.0
$[(L^I)(C_6H_5)_2SnCl_2]$ $C_{19}H_{18}Cl_2N_4Sn$	**7**	90	242-245	46.7 46.4	3.8 3.7	11.5 11.4	9.3	0.5
$[(L^I)(CH_3)SnCl_3]\cdot H_2O$ $C_8H_{13}Cl_3N_4OSn$	**8**	98	270dec	24.0 23.7	3.1 3.2	13.3 13.8	41.4	0.7
$[(L^I)(C_4H_9)SnCl_3]$ $C_{11}H_{17}Cl_3N_4Sn$	**9**	97	257-260	30.4 30.7	4.2 4.0	12.7 13.0	16.9	1.2
$[(L^I)(C_6H_5)SnCl_3]\cdot H_2O$ $C_{13}H_{15}Cl_3N_4OSn$	**10**	90	>380	33.0 33.3	2.9 3.2	11.9 12.0	32.3	0.3
$[(L^I)SnCl_4]\cdot H_2O$ $C_7H_{10}Cl_4N_4OSn$	**11**	98	250dec.	19.4 19.7	2.3 2.1	12.7 13.1	21.2	1.1
$[(L^I)SnBr_4]\cdot 1.5H_2O$ $C_7H_{11}Br_4N_4O_{1.5}Sn$	**12**	28	250dec.	13.8 13.7	1.8 1.8	9.2 9.1	78.9	0.6
$[(L^I)SnI_4]\cdot H_2O$ $C_7H_{10}I_4N_4OSn$	**13**	50	219-221	10.5 10.6	1.4 1.3	7.0 7.1	85.6	0.1
$[(L^I)(CH_3)_2Sn(H_2O)_2](BF_4)_2$ $C_9H_{18}B_2F_8N_4O_2Sn$	**14**	40	250dec.	21.5 21.3	3.7 3.6	10.8 11.2	dec.	
$[(L^T)(CH_3)_2SnCl_2]$ $C_7H_{12}Cl_2N_6Sn$	**15**	90	167-171	22.9 22.7	3.3 3.3	22.7 22.7	9.4	1.1
$[(L^T)(CH_3)_2SnBr_2]$ $C_7H_{12}Br_2N_6Sn$	**16**	95	183-185	18.4 18.3	2.6 2.6	18.1 18.3	41.4	0.6
$[(L^T)(C_6H_5)_2SnCl_2]$ $C_{17}H_{16}Cl_2N_6Sn$	**17**	98	166-167	41.7 41.3	3.2 3.3	16.9 17.0	32.6	0.4
$[(L^T)(CH_3)SnCl_3]\cdot H_2O\cdot 0.5ac^b$ $C_{7.5}H_{14}Cl_3N_6O_{1.5}Sn$	**18**	97	345-346	19.6 20.0	2.6 3.2	18.7 19.2	13.3	0.6
$[(L^T)(C_4H_9)SnCl_3]$ $C_9H_{15}Cl_3N_6OSn$	**19**	90	130dec.	25.2 25.0	3.6 3.5	19.0 19.4	9.8 13.2	1.9 1.3
$[(L^T)(C_6H_5)SnCl_3]\cdot 2H_2O$ $C_{11}H_{15}Cl_3N_6O_2Sn$	**20**	95	250dec.	26.9 27.1	3.1 3.1	16.6 17.2	8.1 18.0	4.0 0.9
$[(L^T)SnCl_4]\cdot H_2O$ $C_5H_8N_6Cl_4OSn$	**21**	97	200dec.	14.3 14.0	2.0 1.9	19.7 19.6	78.4	0.7

[a] In DMSO at room temperature and at molar concentration x 10^{-3}; [b] ac = acetone

One strong absorption at ca. 291 cm^{-1} was also observed in the spectrum of the dichlorodiphenyltinbis(imidazolyl)methane (**7**), whereas two strong absorption were found in the spectrum of the analogous derivative **$[(L^T)Ph_2SnCl_2]$ 17**. These bands were assigned to ν_{sym} Sn-C in markedly distorted trans-R_2 octahedral diphenyl tin(IV) complexes(13).

Table 2
Selected IR data (cm^{-1}) for the Ligand $\mathbf{L^I}$ and for its derivatives **1-14**[a]

Compd	ν(C-H)	1600-1500	<600	other data
$\mathbf{L^I}$	3130w, 3110w	1558w, 1506m		
1	3106m, 3020w	1560m, 1506m	462w, 280w, 240w 226w, 202w	ν(O-H): 3300br δ(OH): 1620br ν(Sn-C): 548m, 520w
2	3128w, 3115w	1593w, 1514s 1505s	385w, 367w, 325w 302w, 279w, 195w	ν(Sn-C): 568s ν(Sn-Cl): 239s δ(Sn-Cl): 190br
3	3128w, 3115w	1592w, 1514s 1505s	382w, 365w, 301w 293w, 279w, 244w 223w	ν(Sn-C): 568s ν(Sn-Br): 185s
4	3121w, 3110w	1505s	381w, 292w, 281w 270w, 251w, 233w 224w	ν(Sn-C): 533s ν(Sn-Br): 180w
5	3143sh, 3120w 3103w	1558m, 1520m	399m, 371w, 348w 325w, 301w, 278m	ν(Sn-C): 623s ν(Sn-Cl): 240s br
6	3107w	1598w, 1519m	395w, 348w, 280w 248w, 227w, 203w	ν(Sn-Cl): 620br ν(Sn-Br): 185br
7	3091w, 3110w	1580w, 1560w 1520m	569w, 458m, 417w 399w, 375w, 352w 324w, 306w, 204s 280w	ν_{as}(Sn-C): 291s ν_s(Sn-C) + ν_{as}(Sn-Cl): 253s, 229s
8	3126w, 3121w 3080w	1519w, 1500br	381m, 326m, 249m	ν(OH): 3300br δ(OH): 1620br ν(Sn-Cl): 299s, 284s 272s ν(Sn-C): 543br ρ(Sn-Cl): 210s, 200s
9	3120w, 3116m	1514m, 1498m	381w, 245w, 229w	ν(Sn-C): 610br ν(Sn-Cl): 293s, 284s 278s
10	3120w, 3110sh	1570m, 1538m	560br, 448m, 373w 363m, 250m, 220m	ν(OH): 3500br δ(OH):1609br ν(Sn-Cl): 309s, 300s ν(Sn-C): 290s, 272sh
11	3120w, 3110sh	1522m, 1510m	552br, 380w 212m, 184m	(OH): 3400br,1630br ν(Sn-Cl):332br, 316br
12	3100w	1571m, 1533m	549br, 399w, 387w 320w, 278w, 255w	ν(OH): 3300br δ(OH):1630br ν(Sn-Br): 238m, 225m 211m, 207m
13	3086w	1570w, 1560w 1540w, 1522w 1508w	540br, 385w, 228w	ν(OH): 3400br δ(OH):1610br ν(Sn-I): 181m
14	3123w, 3110w	1583m, 1557m 1547m	521m, 390br, 355w 351w, 278w	(OH): 3500br,1650br ν(BF_4):1070s br,626s

[a] Nujol mull

We also observed that the Sn-C absorption in diorganotin(IV) complexes tends to shift to higher values upon complexation, possibly due to rehybridation(14).

The triorganotin(IV) derivative **1** shows two medium bands due to ν_{sym} and ν_{asym} (Sn-C) at 548 and 520 cm^{-1} respectively, whereas the monoorganotin **[(L)RSnX$_3$]·yH$_2$O** derivatives exhibit, as expected, a single Sn-C stretching vibration at around 270 cm^{-1} (R = phenyl), 540 cm^{-1} (R = methyl) and 600 cm^{-1} (R = n-butyl) (15).

In the di-, tri- and tetrahalide tin(IV) adducts the ν(Sn-Cl) bands are observed in the regions 250-240, 300-270, and 330-300 cm^{-1} respectively. These absorption are shifted considerably to lower frequencies compared to the parent acids(16), as commonly described in other instances(17). A single broad band is generally observed for the diorganotin adducts of L^{T}, whereas two or three bands for the trihalides **19** and **20**, and a broad absorption for the tetrahalides, consistent with a *cis* structure, analogous to that described for similar complexes of 2,2 bipyridine, 1,10-phenanthroline, 2,2'-bipyrimidine and bis(pyrazol-1-yl)methanes(2,5,6,18).

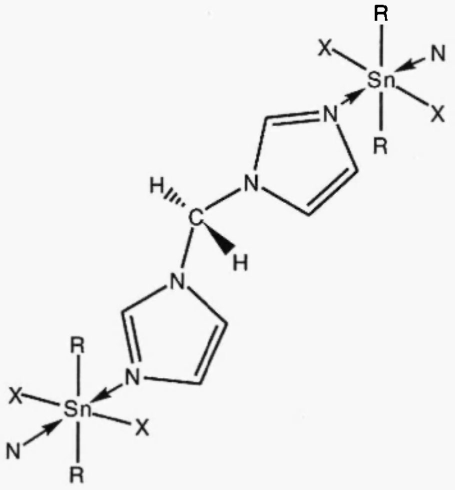

Fig. 2. Structure proposed for dimethyl-, diethyl- and di-n-butyltin(IV) derivatives of **L^{I}**.

Table 3
Selected IR data (cm^{-1}) for the donor **L^{T}** and for itsderivatives **15-21**^{a}

Compd	ν(C-H)	1600-1500	<600	other data
L^{T}	3110w, 3060sh	1599w, 1557m	392w, 384w, 284 216w, 204w	
15	3117w	1547m, 1538m 1502m	353m, 205m, 175m	ν(Sn-C): 575m ν(Sn-Cl): 240s br
16	3116w	1551m, 1541m 1517s	363m, 280w, 247w 197w	ν(Sn-C): 571m ν(Sn-Br): 177m
17	3117w	1570w, 1540w 1518m, 1508m	461m, 382w, 210w 200w, 173w	ν(Sn-C): 291s, 283s ν(Sn-Cl): 233s br
18	3139w, 3110w 3060sh	1539s, 1519br	406w, 200w, 159m	ν(Sn-C): 536s ν(Sn-Cl): 334s, 289s ν(C=O):1697s ν(O-H): 3400br δ(O-H): 1650br
19	3114w	1539m, 1514m	400w, 385w, 184m 172m	ν(Sn-C): 633s ν(Sn-Cl): 315s, 293s 277s
20	3123w, 3019sh	1569w, 1525m	450m, 399w, 382w 232m, 193m, 166m 157m	ν(O-H): 3500br δ(O-H): 1609s br ν(Sn-Cl): 314s ν(Sn-C): 293s, 264sh
21	3119w	1564w, 1527m 1519m	390w, 190w, 165m	ν(O-H): 3550s br δ(O-H): 1614 br ν(Sn-Cl): 320s br

^{a} Nujol mull

Table 4
^1H NMR data for the donor $\mathbf{L^I}$ and for its derivatives **1-14**[a]

No	Solvent	Ligand protons		R-Sn	Other data
		azole	CH_2		
$\mathbf{L^T}$	Acetone	6.9s, 7.3s, 7.9s	6.3s		
	$CDCl_3$	7.0s, 7.1s, 7.7s	6.0s		
	DMSO	6.9s, 7.4s, 7.9s	6.2s		
1	Acetone	7.0s, 7.4s, 8.1s	6.5s	0.6s	68 $\{^2J_{^{119}Sn-^1H}\}$; 64 $\{^2J_{^{117}Sn-^1H}\}$ 2.9s br (H_2O)
	$CDCl_3$	7.0s, 7.1s, 7.7s	6.0s	0.7s	59 $\{^2J_{^{119}Sn-^1H}\}$; 57 $\{^2J_{^{117}Sn-^1H}\}$ 1.7 br (H_2O)
2	Acetone	7.0s, 7.4s, 8.0s	6.4s	1.2s	90 $\{^2J_{^{119}Sn-^1H}\}$; 86$\{^2J_{^{117}Sn-^1H}\}$
	DMSO	6.9s, 7.4s, 8.0s	6.2s	1.0s	115 $\{^2J_{^{119}Sn-^1H}\}$; 110 $\{^2J_{^{117}Sn-^1H}\}$
3	Acetone	7.0s, 7.4s, 8.0s	6.4s	1.2s 1.3s 1.4s	89 $\{^2J_{^{119}Sn-^1H}\}$; 85 $\{^2J_{^{117}Sn-^1H}\}$
4	Acetone	7.0s, 7.4s, 7.9s	6.4s	1.4t	
5	Acetone	7.1s, 7.5s, 8.1s	6.4s	0.9t, 1.4ps 1.8br	
6	Acetone	7.2s, 7.5s, 8.3s	6.5s	0.8t, 1.4ps 1.7m, 1.9m	
7	Acetone	7.0s, 7.4s, 8.0s	6.4s	7.1-7.4m 7.5-8.1m	
	DMSO	6.9s, 7.4s, 8.0s	6.2s	7.0-7.3m 7.7d, 7.9d	96 $\{^2J_{^{119}Sn-^1H}\}$
8	DMSO	7.0br, 7.5br, 8.2br	6.3br	1.0br 1.2br	129 $\{^2J_{^{119}Sn-^1H}\}$ 3.5br (H_2O)
9	DMSO	7.0br, 7.5br, 8.1br	6.3br	0.8t, 1.3ps 1.6m	
10	DMSO	7.3br, 7.6br, 7.8br 8.5br, 9.0br	6.4s 6.5s 6.55s	7.1-7.3m 7.5-7.7m 7.9d	3.6br (H_2O) 110 $\{^2J_{^{119}Sn-^1H}\}$
11	DMSO	7.3s, 7.4s, 7.6s 7.7s, 7.8s, 7.9s 8.6s, 8.7s, 8.75s 8.8s, 9.1s, 9.3s 9.4s	6.5s 6.55s 6.6s		5.0br (H_2O)
12	Acetone	7.8br, 8.0s, 8.7s	6.7s		4.0br (H_2O)
	DMSO	7.7s, 8.0s, 9.3s	6.7s		4.0br (H_2O)
13	DMSO	7.5s, 7.8s, 8.8s	6.5s		3.5br (H_2O)
14	Acetone	7.8s, 8.2s, 9.4s	7.0s	1.4s	2.9br (H_2O)

[a] Chemical shift measured from internal standard tetramethylsilane (TMS), J in Hz;
s = singlet, d = doublet, t = triplet, q = quartet, m = complex pattern, ps = pseudo-sextet,
br = broad.

In the triorganotin(IV) derivative **1**, the tin-chloride stretching frequency is absent. On the basis of previous reports on triorganotin adducts, we have hypothesized an ionic formulation of the type $[(L)R_3Sn]^+[X]^-$(19). The non-electrolyte nature of this compound in DMSO solution is likely due to possibility in solution of the following non-ionic dissociation:

$$[(L^I)(CH_3)_3Sn]^+[X]^- + n\,DMSO \longrightarrow [(DMSO)_n(CH_3)_3SnX] + L^I \qquad (7)$$

We assigned the broad band at ca. 230 cm^{-1} in the spectrum of compound **12**, and the medium absorption at ca. 180 cm^{-1} in the spectrum of **13**, to ν(Sn-Br) and ν(Sn-I) stretching vibration respectively(20).

Although it is difficult to assign values for the Sn-N frequencies, it has been reported that they lie between 600 and 200 cm^{-1}(21). In our complexes new bands which appeared between 380 and 280 cm^{-1} could be assigned to ν(Sn-N) by comparison with literature data(18,21).

^1H and ^{119}Sn NMR data

The ^1H NMR spectra of derivatives **1-21** in acetone solution, or when not possible in dimethylsulphoxide (Tables 4 and 5), support the formulae proposed and show that the organic ligand has not undergone any structural change. The spectra of the tri- and diorganotin(IV) derivatives **1, 2, 3, 4, 5, 6, 7, 15** and **16** indicate that the ligand is completely released in acetone or DMSO: the observed signals are almost identical to those of the free ligand in the same solvent, this giving further support for the occurrence of reaction ***8***:

$$[(L)R_nSnX_{4-n}]\cdot yH_2O + x(\text{solvent}) \longrightarrow [(\text{solvent})_xR_nSnX_{4-n}] + L + yH_2O \quad (\mathbf{8})$$

Table 5
^1H NMR data for the donor $\mathbf{L^T}$ and for its derivatives **15-21**[a]

No	Solvent	Ligand protons		R-Sn	Other data
		azole	CH_2		
$\mathbf{L^T}$	Acetone	7.9s, 8.7s	6.7s		
	DMSO	8.1s, 8.9s	6.7s		
15	Acetone	7.9s, 8.7s	6.7s	1.2s	84 $\{^2J_{^{119}Sn-^1H}\}$; 80$\{^2J_{^{117}Sn-^1H}\}$
	Acetone	8.1s, 8.9s	6.8s	1.2s	87 $\{^2J_{^{119}Sn-^1H}\}$; 83$\{^2J_{^{117}Sn-^1H}\}$
	DMSO	8.0s, 8.9s	6.6s	1.0s	114 $\{^2J_{^{119}Sn-^1H}\}$; 110$\{^2J_{^{117}Sn-^1H}\}$
16	Acetone	8.0s, 8.7s	6.7s	1.5s	82 $\{^2J_{^{119}Sn-^1H}\}$; 79$\{^2J_{^{117}Sn-^1H}\}$
17	DMSO	8.0s, 8.1s	6.6s	7.2-7.5m	116 $\{^2J_{^{119}Sn-^1H}\}$; 112$\{^2J_{^{117}Sn-^1H}\}$
		8.8s, 8.9s	6.7s	7.9d	
18	DMSO	8.1s, 8.15s	6.6s	1.0br	2.1s $[(CH_3)_2CO]$
		8.8s, 8.9s	6.7s	1.3br	3.4s (H_2O)
	Acetone	8.2br, 9.0br, 9.2br	6.8s	1.5 s br	2.9s (H_2O)
			7.0s		
			7.1s		
19	DMSO	8.1br, 8.9br	6.7br	0.9br, 1.3br	
				1.6br	
20	DMSO	8.0s, 8.1s	6.5s	7.2-7.5m	3.6br (H_2O)
		8.8s, 8.9s	6.6s	7.7br	
21	DMSO	8.0s, 8.1s, 8.8s	6.6s		5.0br (H_2O)
		8.9s, 9.0s	6.7s		

[a] Chemical shift measured from internal standard tetramethylsilane (TMS), J in Hz;
s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, ps = pseudo-sixtet,
br = broad.

In the case of the tri- and tetrahalide tin(IV) adducts **8, 9, 12, 13** and **19** when complexation occurs, there are changes in the chemical shifts of the protons in the ligand: a downfield displacement of all the signals was always observed; the shift, generally not negligible, is additional evidence of the existence of complexes in solution. Additional evidence for this hypothesis is the value of the $J(^{119}Sn-^1H)$ coupling constant: for example $^2J(^{119}Sn-^1H)$ =129 Hz in **8**: this value is comparable with those reported in literature for other (N_2-donors)tin(CH_3)Cl_3 adducts(22).

The complexes **10, 11, 17, 18, 20** and **21** may undergo different equilibria in DMSO solution, as indicated also by conductivity data. In fact in the ^1H spectra of these complexes more than one set of signals is observed for the imidazole or triazole ring protons and also for the bridging CH_2 group. Since the intensity ratio between the set is often different from the unity, the presence of more than one species in solution must be assumed, in keeping with another line of evidence.

In fact, in several ^{119}Sn NMR spectra, those of **8-11** (Table 6), more than one signal is observed, namely three for **8**, two for **9**, eight for **10** and five for **11**. In the spectrum of **10**, the signals at -508 and -510 ppm corresponds to those observed for $PhSnCl_3$ in the same solvent and may be attributed to the existence in DMSO solution of the $[(DMSO)_2PhSnCl_3]$ complex[(23)], thus providing additional evidence against dissociation into the starting reagents, whereas the signals at --497 is likely due the complex **$[L^T)PhSnCl_3]$**. The ^{119}Sn NMR spectrum of **10** exhibits also signals at -402, -469, -624 and -668 and -675 ppm: in fact the dissociation product $PhSnCl_3$ might undergo a redistribution reaction producing $SnCl_4$ and Ph_2SnCl_2 which would afford the derivatives **$[L^T)Ph_2SnCl_2]$**, **$[L^T)SnCl_4]$**, **$[DMSO)_2Ph_2SnCl_2]$** and **$[DMSO)_2SnCl_4]$**, by complexation with L^T or DMSO. Additional evidence for this hypothesis is the spectrum of **11**, where the same signals at -624, -668 and -675 ppm were detected.

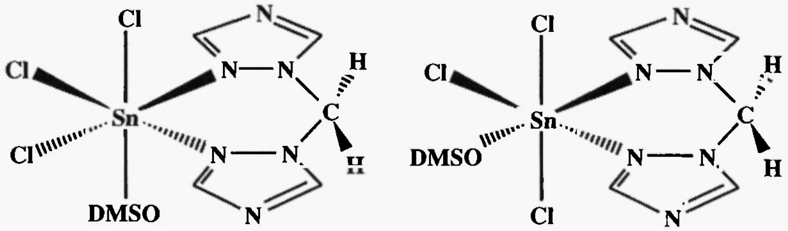

Fig. 3. Facial and meridional isomer possible for **$[(L^T)(DMSO)SnCl_3]^+[Cl]^-$**.

Table 6

^{119}Sn NMR data (DMSO-d_6) of derivatives **8-11**, **17** and **21**[a]

Compound	No	δ(ppm)
$[(L^T)(CH_3)SnCl_3]\cdot H_2O$	**8**	-451, -454, -468
$[(L^T)(C_4H_9)SnCl_3]$	**9**	-452br, -465
$[(L^T)(C_6H_5)SnCl_3]\cdot H_2O$	**1 0**	-402, -469, -497 -508, -510, -624 -668, -675
$[(L^T)SnCl_4]\cdot H_2O$	**1 1**	-621, -624, -626 -668, -675
$[(L^T)(C_6H_5)_2SnCl_2]$	**1 7**	-402
$[(L^T)(SnCl_4]\cdot H_2O$	**2 1**	-625, -668

[a] It was not possible to record ^{119}Sn NMR spectra of compounds **12**, **13**, **14**, **18**, **19** and **20** due to the poor solubility of the sample (ca. 10^5 cycles acquired). ^{119}Sn NMR spectra of derivatives **1-6**, **15** and **16** are almost identical to those of the not coordinate acceptor in the same solvent, this giving further support for the occurrence of reaction *8*.

When a DMSO-d_6 solution of **10** or of **18** was heated at 320°K, several additional signals at ca -200 and -500 ppm appeared, which are attributed to hydrolysis products.

In the ^1H and ^{119}Sn NMR spectra of compound **21**, two and three set of signals are respectively observed. They are accounted for in term of the presence of an equilibrium of type *3*: one set likely correspond to the unsolvated molecule **$[(L^T)SnCl_4]\cdot H_2O$** and the others to the solvated cation **$[(L^T)(DMSO)_nSnCl_3]^+[Cl]^-$**, for which, if n = 1, a facial and a meridional isomer are possible (Fig. 3). Tables 4 and 5 also show the J(Sn-C-H) coupling constants. A Fermi contact mechanism govern the coupling between Sn and H[(24)], therefore the more *s* character with which the Sn atom engages the organyl groups, the higher, the values of J will be. The J values in complexes **8** and **10** are higher than those reported for the uncomplexed Lewis acid[(25)]. This is accounted for by the increased covalency of the Sn-C bond, which implies a higher degree of *s* orbital participation. This interpretation agrees also with the fact that the IR spectra of **8** and **10** show an increase in ν(Sn-C) upon complexation[(26)].

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References

(1) P. G. Harrison, T. J. King and J. A. Richards, *J. Chem. Soc., Dalton Trans.*, (1974) 1723; P. Ganis, V. Peruzzo and G. Valle, *J. Organomet. Chem.*, **256**, (1983) 245; V. G. Kumar Das, Y. C. Keong, C. Wei, P. J. Smith and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, (1987) 129.
(2) C. Pettinari, A. Lorenzotti, G. Sclavi, A. Cingolani, E. Rivarola, M. Colapietro and A. Cassetta, *J. Organomet. Chem.*, **496**, (1995) 69
(3) S. G. Ward, R. C. Taylor, A. J. Crowe, J. Balzarini and E. De Clercq, *Appl. Organomet. Chem.* ,**3**, (1989) 431.
(4) A. J. Crowe, P. J. Smith and G. Atassi, *Inorg. Chim. Acta*, **93**, (1984) 179; C. J. Cardin and A. Roy, *Inorg. Chim. Acta*, **107** (1985) 57.
(5) G. Gioia Lobbia, A. Cingolani, D. Leonesi, A. Lorenzotti and F. Bonati, *Inorg. Chim. Acta*, **130** (1987) 203.
(6) G. Gioia Lobbia, F. Bonati, A. Cingolani, D. Leonesi and A. Lorenzotti, *J. Organomet. Chem.*, **359** (1989) 21.
(7) M. R. Grimmett, Imidazoles and their benzo derivatives: (i) structure, in *Comprehensive Heterocyclic Chemistry* [Edited by A. R. Katritzky and C. W. Rees (Editors in Chief), and K. T. Potts (Ed.)], Vol. 5, Part 4A, p. 345. Pergamon press, Oxford (1984).
(8) G. Gioia Lobbia and F. Bonati, *Synth. React. Inorg. Met.-org. Chem.*, **18** (1988) 551.
(9) A. Lorenzotti, A. Cingolani, G. Gioia Lobbia and D. Leonesi, *Gazz. Chim. Ital.*, 117 (1987) 191; D. Leonesi, A. Cingolani, G. Gioia Lobbia, A. Lorenzotti and F. Bonati, *Gazz. Chim. Ital.*, 117 (1987) 491.
(10) G. Nieuwpoort, J. G. Vos and W. L. Groeneveld, *Inorg. Chim. Acta*, **29**, (1978) 117.
(11) L. E. Moore, R. B. Gayhart and W. E. Bull, *J. Inorg. Nucl. Chem.*, **26**, (1964), 896.
(12) W. F. Edgell and C. H. Ward, *J. Mol. Spectrosc.*, **8**, (1962), 343; J. K. Sandhu, G. Kaur, J. Holecek and A. Licka, *J. Organomet. Chem.*, **345**, (1988), 51.
(13) J. R. May, W. R. McWhinnie and R. C. Poller, *Spectrochim. Acta*, **27A**, (1971), 969; A. L. Smith, *Spectrochim. Acta*, **24A**, (1967), 695; M. S. Dance, W. R. McWhinnie and R. C. Poller, *J. Chem. Soc. Dalton Trans.* (1976), 2349.
(14) R. J. H. Clark, A. G. Davies and R. J. Puddephatt, *J. Chem. Soc. A*, (1968), 1828.
(15) A. L. Smith, *Spectrochim. Acta. Sect. A*, **24**, (1968) 695.
(16) G. F. de Sousa, C. A. L. Filgueiras, M. Y. Darensbourg and J. H. Reibenspies, *Inorg. Chem.* , **31**, (1992), 3044.
(17) B. Alberte, A. Sanchez Gonzalez, E. Garcia, J. S. Casas, J. Sordo and E. E. Castellano, *J. Organomet. Chem.*, **338**, (1988),187.
(18) N. Ohkaku and K. Nakamoto, *Inorg. Chem.*, **12**, (1973) 2440; F. Caruso, M. Giomini, A. Giuliani and E. Rivarola, *J. Organomet. Chem.*, **506** (1996) 67.
(19) T. S. Basu Baul, D. Dey, D. D. Mishra, W. L. Basaiawmoit and E. Rivarola, J. Organomet. Chem., **447**,(1993), 9.
(20) M. F. Farona, *Inorg. Chem.* , **14**, (1975) 2020.
(21) T. Tanaka, M. Komura, Y. Kawasaki and R. Okawara, *J. Organomet. Chem.*, **1**, (1964), 484; V. G. Kumar Das, Y. Chee-Keong and P. Smith, *J. Organomet. Chem.*, **327**, (1987), 311.
(22) R. Visalakshi, V. K. Jain, S. K. Kulshreshtha and G. S. Rao, *Inorg. Chim. Acta*, **118**, (1986),119; C. Pettinari, F. Marchetti, A. Cingolani and S. Bartolini, *Polyhedron*, **15**, (1996), 1263.
(23) C. Pettinari, *unpublished results.*
(24) W. F. Lockhart and T. P. Manders, *J. Am. Chem. Soc.*, **109**, (1987), 7015.
(25) B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.*, **16**, (1985), 73.
(26) K. Kawakami and R. Okawara, *J. Organomet. Chem.*, **6**, (1966), 249.

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