Tin(IV) and Organotin(IV) Adducts of Bis(1-pyrazolyl)methane

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Abstract

Bis(pyrazol-1-yl)methane, (L-L), reacts with tin(IV) or organotin(IV) halides yielding (L-L)SnX_mR_{4-m} (X = Cl, Br, I; m = 4, 3 or 2 but not 1; R = methyl or phenyl). NMR spectra show that the compounds are fluxional, while combined molecular weight determinations and conductivity data show that in acetone solution the molecules obtained dissociate readily into the starting materials.

Introduction

In a preceding paper of ours [1] several mercury(II) adducts of bis(1-pyrazolyl)methane, L-L, were described. This organic molecule is the simplest member of the family of the poly-pyrazolylalkanes; it is a flexible, heteroaromatic analogue of the well established [2], and more rigid bidentate ligands 2,2′-bipyridine or *ortho*-phenanthroline. In addition to other work on the interaction between compounds belonging to the second group and the same or other, related ligands [3], it was decided to continue our investigation using tin(IV) acceptors since these are well known Lewis acids, and to include organotin(IV) species since their acidity is inversely proportional to the number, and type, of organic substituents. A few organotin(IV) derivatives had been described previously and a structure proposed [4], which will be discussed here together with our results.

Results and Discussion

The interaction between the ligand and tin compounds was generally carried out in diethylether and gave the adducts listed below

$$SnX_mR_n + \text{L-L} = (\text{L-L})SnX_mR_n$$

Compound no.	1	2	3	4	5	6	7	8
X	Cl	Br	I	Cl	Cl	Cl	Br	Cl
m	4	4	4	2	3	3	2	2
R				Me	Me	Ph	Ph	Ph
n				2	1	1	2	2

The analytical data (Table I) showed that only 1:1 adducts were isolated even in the presence of excess ligand. With the exception of **6**, with retained *ca.* ¼ diethylether, the result was independent of the solvent employed. For example **1** was also obtained from ethanol but, on the other hand, even from hydrocarbon solution, no adduct was isolated from trimethyl- or triphenylchlorotin, in agreement with the decreasing acid character of tin(IV) upon increasing the number of alkyl substituents.

All the compounds obtained are solid. They are colourless with the exception of **3** and **4**, which are blood red and yellow, respectively. They are not electrolytic in acetone, thus ruling out in this solvent ionic structures, e.g. $[Sn(\text{L-L})_3][SnCl_6]_2$, or equilibria such as

$$(\text{L-L})SnR_nX_{4-n} + \text{solvent} = [(\text{L-L})SnR_nX_{4-n-1}(\text{solvent})]^+ + X^-$$

According to molecular weight determinations by osmometry the compounds are extensively dissociated in acetone solution and totally dissociated in dimethylsulphoxide

$$(\text{L-L})SnR_nX_{4-n} + \text{solvent} = (\text{solvent})_2SnR_nX_{4-n} + \text{L-L}$$

For example in compound **8**, Ph_2SnCl_2(L-L), the ratio *n* between the molecular weight and the formula weight is 0.73–0.76 in acetone but only 0.49 in dimethylsulphoxide; similar results are found for

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TABLE I. Some Physical Data of the Compounds Prepared

Compound		Melting point (°C)	Yield (%)	Elemental analyses[a] (%)			Specific conductivity[b] (ohm^{-1} cm^2 mol^{-1})	
				C	H	N		
$C_7H_8N_4SnCl_4$	(1)	297–299	92	20.25 (2058)	2.09 (1.97)	13.85 (13.71)	(1.03)	20.87*
$C_7H_8N_4SnBr_4$	(2)	274–275	64	14.69 (14.34)	1.48 (1.04)	9.76 (9.55)	(0.98)	10.92
$C_7H_8N_4SnI_4$	(3)	160–162	35	10.88 (10.86)	1.03 (1.04)	7.26 (7.24)	(1.00)	69.27
$C_9H_{14}N_4SnCl_2$	(4)	121–122	48	29.39 (29.39)	3.79 (3.84)	15.40 (15.23)	(1.01)	4.69
$C_8H_{11}N_4SnCl_3$	(5)	250–252	96	24.80 (24.75)	2.91 (2.86)	14.66 (14.43)	(1.06) (1.06)	19.60[c] 29.29*
$C_{13}H_{13}N_4SnCl_3 \cdot \frac{1}{4}(C_2H_5)_2O$	(6)	300	86	34.98 (35.56)	3.13 (3.30)	12.08 (11.84)	(0.99)	9.13
$C_9H_{14}N_4SnBr_2$	(7)	127–129	74	23.43 (23.67)	3.04 (3.09)	12.40 (12.27)	(0.98)	5.49
$C_{19}H_{18}N_4SnCl_2$	(8)	180–182	84	46.10 (46.39)	3.68 (3.69)	11.61 (11.39)	(1.01)	5.55

[a] Calculated values in parentheses. [b] Acetone solution at room temperature and at the molar concentration × 10^{-3} indicated in parentheses. The solvent was DMSO for the starred compounds. [c] Additional conductivity data in acetone: 8.07, 12.85, 23.53, and 41.60 at molar concentration (×10^{-3}) 3.40, 1.7, 0.85, and 0.43 respectively.

TABLE II. Molecular Weight Determination by Osmometry

Compound	Formula weight *FW*	Solvent	Concentration (%, *w*/*w*)	Molecular weight *MW*	*MW*/*FW*
1	408.7	DMSO	3.22	181	0.44
2	586.5	DMSO	3.29	211	0.36
3	774.5	acetone	0.75[a]	384	0.50
			1.10[b]	412	0.53
4	367.8	acetone	1.21[a]	178	0.49
			0.90[b]	188	0.51
5	388.3	acetone	3.27	271	0.70
		DMSO	3.68	179	0.46
6	468.8	acetone	0.66[a]	312	0.67
			0.87[b]	347	0.74
7	456.7	acetone	0.78[a]	221	0.48
			1.52[b]	238	0.52
8	492.0	acetone	0.91[a]	358	0.73
			1.05[b]	374	0.76
		DMSO	2.52	242	0.49

[a] Determination with thermistor probes for electrically non conductive solutions. [b] Determination with special isolated thermistor probes.

compound **5**. If the values of *n* for our compounds are compared, it is evident that in acetone solution the less dissociated adducts are those where there are electronegative substituents on the tin atom, such as in **5**, **6**, or **8**. This is noticeably different to the zinc, cadmium, or mercury derivatives already reported, where the *n* value in acetone or chloroform is nearly unity for all the 1:1 adducts obtained. The different extent of the dissociation of the 1:1 adducts between the group IIB elements on the one hand and tin(IV) on the other, does not mean that the latter is a weaker Lewis acid than the former elements, since it should be noticed that with tin(IV) a higher coordination number (5 or 6) is reached than with the former elements; and, indeed, when 2:1 non-ionic zinc or cadmium adducts [3a] are considered, molecular weight determinations showed that they too are extensively dissociated.

TABLE III. Proton Magnetic Resonance Data

Compound	Solvent	Ligand[a]			Others[h]
		$>CH_2$	C(4)–H	C(3) or C(5)–H	
L-L	$(CD_3)_2CO$	6.54s	6.39t (1.8)	7.61d (1.5) 7.98d (1.8)	
	$CDCl_3$[b]	6.30s	6.26t (1.2)	7.55d (1.8) 7.63d (2.4)	
	DMSO-d_6[b]	6.39s	6.28t (1.8)	7.49d (1.4) 7.93d (2.1)	
1	DMSO-d_6	6.40s	6.30t (1.2)	7.50d (1.8) 7.93d (2.0)	
2	$(CD_3)_2CO$	7.47s	6.75t (2.7)	8.38s, broad 8.67s, broad	
3	$(CD_3)_2CO$	7.23s	6.63t (2.2)	8.20d (3.0) 8.49d (2.6)	
4	$(CD_3)_2CO$	6.40s	6.30t (1.6)	7.50s, broad 7.87d (2.7)	Me: 1.22s (80; 86)
	$CDCl_3$[c]	6.31s	6.27t (2.5)		Me: 1.20s (66; 69)
5	$(CD_3)_2CO$	6.98s	6.51t (1.5)	8.03d (1.7) 8.11d (2.6)	Me: 1.44s[d]
6	$(CD_3)_2CO$	7.11s	6.54t (1.9)	8.23d (2.5)	Ph: 7.56–7.32m 7.88–8.15t[e,f]
7	$CDCl_3$	6.41s	6.29t (1.4)	7.50s 7.85d (2.5)	Me: 1.45s (78; 84)
8	DMSO-d_6	6.43s	6.29t (1.5)		[g]

[a] δ in ppm from internal TMS: s = singlet, d = doublet, t = triplet. *J* in parentheses in Hz. [b] From ref. 7. [c] From ref. 4. [d] *J*(Sn–H) not observed, the compound being sparingly soluble. [e] One of the signal overlap with phase of the phenyl group. [f] There is also a triplet and a quartet at 1.13 and 3.42 ppm (*J* = 7 Hz) due to clathrated diethylether. [g] Phenyl and part of the pyrazole ring protons overlap (7.90–8.05); (7.39–7.60). [h] The couples of values listed between brackets in this column are $J(^{117}Sn–H)$ and $J(^{119}Sn–H)$, in the order.

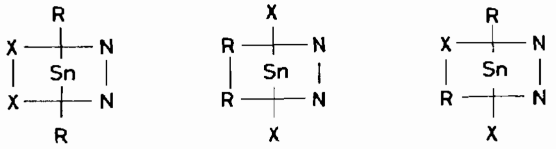
TABLE IV. ^{13}C NMR Data[a]

Compound	Solvent	C(3)	C(4)	C(5)	CH_2	Others
L-L	$(CD_3)_2CO$	140.2	106.4	130.1	65.1	
	DMSO-d_6[b]	140.1	106.3	130.5	64.4	
	$CDCl_3$	140.6	107.0	129.5	65.1	
	CD_3OD	141.4	107.8	130.8	65.4	
1	DMSO-d_6	140.0	106.2	130.5	64.2	
2	DMSO-d_6	139.9	106.2	130.5	64.2	
3	$(CD_3)_2CO$	140.1	106.4	133.6	62.7	
4	$(CD_3)_2CO$	140.3	106.5	130.2	65.0	Me: 11.7
5	CD_3OD	142.2	108.0	132.1	65.7	Me: 22.7
6	CD_3OD	141.7	107.7	130.2	65.4	Ph: 134.7 131.8 129.0
7	$CDCl_3$	140.8	107.2	129.7	65.2	Me: 7.7
8	DMSO-d_6	140.4	106.6	130.9	64.5	Ph: 135.0(*J* = 70) 128.2 127.7(*J* = 121)

[a] Chemical shifts in ppm from internal TMS. [b] From ref. 5a.

The ^1H and ^{13}C NMR spectra (Tables III and IV respectively) were recorded for all the compounds isolated. The choice of the solvent was dictated by solubility, the order of preference being $CDCl_3$, $(CD_3)_2CO$ and $(CD_3)_2SO$. In any of these solvents the spectra were in agreement with the requirement of the formulae proposed, thus ruling out any rearrangement or transformation of the organic part of the molecules **1**–**8**. Nevertheless, comparison between the values of chemical shifts related to the same type of protons in different compounds can be carried out only if the spectra are recorded in the same solvent: in our case chloroform dissolves only a few compounds, in acetone more or less extensive dissociation takes place, while dimethylsulphoxide has a levelling influence owing probably to its tendency to displace ligands from the coordination sphere.

In keeping with the extensive dissociation of the adducts, in the proton NMR spectra of our compounds only one methyl singlet (with accompanying $^{117}Sn-H$ and $^{119}Sn-H$ satellites) and one set of L-L signals were observed, thus pointing to a fast equilibrium between the three different geometric isomers possible for **4**, **7**, or **8**:



In addition the metal $(N\text{-}N)_2C$ ring is expected to be in the boat configuration established through X-ray crystal structure, see for example ref. 5. As a consequence, in any of the said geometric isomers, possible for **4**, **7**, or **8**, as well as for the only isomer allowed when X = R (compounds **1**, **2**, and **3**), the two N-CH_2-N hydrogens ought to be different. Indeed an AB pattern was reported for $(L\text{-}L)PtCl_2$ [6], in agreement with the well-established kinetic inertness of platinum(II). On the contrary, in all the tin compounds described here or elsewhere [4], as well as in many other zinc, cadmium, or mercury(II) adducts [1, 3], the N-CH_2-N hydrogens are always found to be magnetically equivalent, at least at room temperature, so that even when dissociation is not the cause, a rapid boat inversion must be assumed, probably passing through Sn–N bond breaking. For all these reasons a fluxional behaviour is likely for all our pseudo-octahedral compounds, so that the choice [4] between any of the possible isomers is reasonable only in the solid state. Similar considerations are also likely for the five coordinated complexes $(L\text{-}L)SnRCl_3$.

Experimental

The samples were pumped to constant weight (20°, *ca.* 0.1 torr). Carbon, hydrogen, and nitrogen analyses were carried out in our Department or by Mr. A. Canu at the University of Sassari. The molecular weight determinations were performed at the Pascher's Mikroanalitisches Laboratorium, Remagen, F.R.G. Infrared spectra from 4000 to 250 cm^{-1} were recorded on a Perkin-Elmer 457 instrument (Table V). ^1H and ^{13}C NMR spectra were recorded on a Varian EM-390 and FT80A instruments operating at room temperature (90 and 20 MHz).

TABLE V. Selected Infrared Data (Nujol mull) (cm^{-1})

Compound	(C–H) azole	1500–1600	<500
L-L	3135m 3110m	1520m 1510sh	395s 360m
1	3140w 3120m 3040w	1520w	470w 420w 380v 330m[a] 280vw
2	3140w 3120m	1520w	420m 370w
3	3160w 3140vw 3120w	1520w	470w 400s 350w 330vw
4	3160w 3140w 3130w	1520m 1510w	410s 360w 320w
5	3160vw 3120w	1520m 1510w	400m 360w 330m[a] 290m 280m
6	3140vw 3120w 3110w	1570w 1520m	460m 410m 370w 300s,br[a] 260m
7	3120w	1520w	420m 370w
8	3140w 3130vw 3110w	1570w 1520w,br	470m 460m 400w 350vw 320vw 290m,br[a] 260m

[a] Sn–Cl stretching vibration.

[Bis(pyrazol-1-yl)methane] tetrachloridetin (1)

An ethanol solution (20 ml) of the ligand (4.0 mmol) was added to a stirred ethanol solution of $SnCl_4$ (20 ml, 2.05 mmol). A white precipitate was obtained immediately and compound **1** was filtered and washed. Compounds **2**–**8** were obtained in a similar way from an ethereal solution.

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