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A Mössbauer study of tin(IV) and organotin(IV) adducts of bis(pyrazolyl)methane-type ligands

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Abstract

The ^{119m}Sn Mössbauer parameters at 4.2 K of a series of adducts of general formula $R_nSnX_{4-n}(L–L)$ [$n = 0, 1,$ or 2; X = Cl, Br, or I; L–L = a bis(pyrazol-1-yl)methane type ligand] are reported and discussed. They are shown to provide information on bonding and on coordination in the solid state.

Introduction

Even though the poly(pyrazolyl)alkanes are versatile ligands, only a few reports of adducts of SnX_4, $RSnX_3$, R_2SnX_2 with poly(pyrazolyl)methane-type ligands have been published [1,2]. These ligands, since their discovery by Trofimenko [3], have been shown to be flexible, heteroaromatic analogues of the well established and more rigid bidentate ligands 2,2′-bipyridine and 1,10-phenanthroline [4]. As a part of our search [5] for poly(pyrazolyl)alkane derivatives of non-transition elements [6], compounds of general formula $R_nSnX_{4-n}(L–L)$ have been prepared and characterized ($n = 0$, 1, or 2; X = Cl, Br or I; R = Me or Ph; L–L = bis(pyrazol-1-yl)methane; L′–L′ = bis(3,5-dimethylpyrazol-1-yl)methane; L″–L″ = 2,2-bis(pyrazol-1-yl)propane.

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An additional reason for investigating the title compounds lies in the report that some of their derivatives such as six-coordinate dialkyl- and diaryl-di(pseudo)-halidetin complexes with bidentate N-donors show antitumour [7–9] and antiviral [8b] activity. In the octahedral structures reported for these complexes, the halogen ligands are *cis*, and this appears to be an essential requirement for anticancer activity, as in platinum complexes. Understanding the mechanism of activity of these adducts requires an understanding of their structure and isomerism. Other compounds of organotin(IV) species with poly(pyrazolyl) borates [10–12] and with diamines (for example, 1,2-ethylenediamine and 1,4-butanediamine [13]) have been described and characterized, especially in the solid state, through IR and Mössbauer spectra. However, the toxicity of the resulting compounds was found to be too high for medical applications [14].

In the absence of X-ray crystal structure determinations, ^{119m}Sn Mössbauer spectroscopy may give insights into the bonding and coordination geometry in the solid state.

Results and discussion

The Mössbauer isomer shifts (IS), quadrupole splittings (QS) and average linewidths at half-maximum (LW), are reported in Table 1. There is a linear relationship between QS and IS values whose slope shows that the tin coordination number is greater than four. This excludes the presence of starting materials in the samples studied.

Table 1

^{119m}Sn Mössbauer parameters at 4.2 K

Compound [a]	IS [b] (mm/s)	QS (mm/s)	LW (mm/s)
1 $SnCl_4$(L–L)	0.37(1)		0.83(1)
2 $SnCl_4$(L′–L′)	0.37(1)		0.90(1)
3 $SnBr_4$(L–L)	0.63(1)		0.84(1)
4 SnI_4(L–L)	1.00(8)		0.94(7)
5 $SnBr_3OH$(L′–L′)	0.65(1)	0.41(1)	0.82(2) (69%) [c]
	0.32(3)	0.92(3)	0.88(2) (31%) [c]
6 $SnCl_4$(L″–L″)·H_2O	0.34(1)		0.88
7 $MeSnCl_3$(L–L)	0.86(1)	2.05(1)	1.08(9)
8 $MeSnCl_3$(L′–L′)	0.92(1)	2.12(1)	0.94(1)
9 $PhSnCl_3$(L–L)·1/4Et_2O	0.78(1)	1.88(1)	0.85(1)
10 $PhSnCl_3$(L″–L″)	0.78(1)	1.57(1)	1.05(4)
11 Me_2SnCl_2(L–L)	1.40(1)	4.17(1)	0.81(9)
12 Ph_2SnCl_2(L–L)	1.31(1)	3.73(1)	0.81(9) (89%) [c]
	0.83(9)	1.94(9)	0.89(9) (11%) [c]
13 Ph_2SnCl_2(L′–L′)	1.33(1)	3.73(1)	0.82(9)
14 Me_2SnBr_2(L–L)	1.50(1)	4.16(1)	0.89(1)

[a] L–L = bis(pyrazol-1-yl) methane; L′–L′ = bis(3,5-dimethylpyrazol-1-yl)methane; L″–L″ = 2,2-bis(pirazol-1-yl)propane. [b] Relative to SnO_2. [c] Percentage of the tin site calculated by Mössbauer resonance area.

Table 2

Observed and calculated quadrupole splitting

No.	Adduct	Observed	Calculated [a]			Octahedral geometry [g]
1	$SnCl_4$(L-L)			−0.16		*trans*-Cl, Cl
2	$SnCl_4$(L′-L′)			−0.16		*trans*-Cl, Cl
3	$SnBr_4$(L-L)			−0.16		*trans*-Br, Br
4	SnI_4(L-L)			+0.12		*trans*-I, I
5	$SnBr_3OH$(L′-L′)	0.41		−0.31		*trans*-N, OH
		0.92		−0.52		*trans*-Br, OH
6	$SnCl_4$(L″-L″)H_2O			−0.16		*trans*-Cl, Cl
7	$MeSnCl_3$(L-L)	2.05	+1.90 [b]	+2.15 [c]		*trans*-RN
8	$MeSnCl_3$(L′-L′)	2.12	+1.90 [b]	+2.15 [c]		*trans*-RN
9	$PhSnCl_3$(L-L)1/4Et_2O	1.88	+1.74 [b]	+1.83 [e]		*trans*-RN
10	$PhSnCl_3$(L″-L″)	1.57	+1.74 [b]	+1.83 [e]		*trans*-RX
11	Me_2SnCl_2(L-L)	4.17	+3.96 [f]	−2.22 [e]	−1.92 [d]	*trans*-RX
12	Ph_2SnCl_2(L-L)	3.73	+3.64 [f]	−2.06 [e]	−1.83 [d]	*trans*-RR
		1.94	+3.96 [f]	−2.06 [e]	−1.83 [d]	*trans*-NX
13	Ph_2SnCl_2(L′-L′)	3.73	+3.96 [f]	−2.06 [e]	−1.83 [d]	*trans*-RR
14	Me_2SnBr_2(L-L)	4.16	+3.96 [f]	−2.22 [e]	−1.92 [d]	*trans*-RR

[a] Calculated by using the literature [16] octahedral partial quadrupole splittings, in mm/s, Cl = Br = OH = 0.00, I = −0.14, H_2O = 0.18, Me = −1.03, Ph = −0.95. In addition, −0.08 the value of 2,2′-bipyridine, as a working approximation for the unknown bis(pyrazol-1-yl)methane-type ligands and −0.33 for unidentate ones. [b] *trans*-RX. [c] *trans*-RN. [d] *trans*-NX. [e] *trans*-XX. [f] *trans*-RR. [g] The denomination of the geometric isomers is based on V_{zz} direction.

In most cases the width of Mössbauer lines are close to the minimum observable of 0.63 mm/s (Table 1). This shows that all tin atoms have the same or very similar environments.

In the inorganic series of compounds **1–4**, the *s*-electron density at the tin nucleus shows the expected trend with halogen electronegativity, indicating that there is no structural change along the series. The electronegativity trend is also evident in Me_2SnCl_2(L–L) (**11**) and Me_2SnBr_2(L–L) (**14**).

The decrease in the *s*-electron density at the tin nucleus and in the asymmetry of the *p*-orbital population, observable in the pairs of adducts **7**/**9** and **11**/**12**, is consistent with the decreasing inductive effect of Ph in comparison with Me.

The magnitude of the IS and QS values of the bis(pyrazol-1-yl)methane-type adducts R_nSnX_{4-n}(L–L) is determined mainly by *n*. For the same *n*, the nature of the ligands L–L affects the Mössbauer parameters in a different way. In order to understand the chemical behaviour of the L–L-type ligands, we examined all the isomers in the octahedral and trigonal bipyramidal geometries using the point-charge model, taking into account that L–L might be bidentate or unidentate.

The Mössbauer spectra of adducts **1–4** are characterized by a single line with isomer shifts comparable to the values reported for octahedral derivatives of inorganic tin(IV) halides [15]. By using the point-charge method with the partial quadrupole splitting values [16] reported in the footnote of Table 2, it is possible to show that these compounds contain the bidentate bis(pyrazol-1-yl)methane-type ligand in a *cis*-octahedral tin environment. The alternative, *i.e.* unidentate L–L in the two trigonal bipyramidal tin sites, is ruled out since only one line is present in the Mössbauer spectra. For the same reason, and because of the bis(pyrazol-1-yl)methane geometry, a bidentate bridging tin coordination, analogous to that proposed for the pyrazine-containing adducts $SnX_4 \cdot$ pyz [17], can be excluded.

Comparison of the spectra of the complexes $[SnCl_6]^{2-}$, $[SnBr_6]^{2-}$, and $[SnI_6]^{2-}$, with singlet IS 0.43, 0.75 and 1.35 mm/s, respectively [18], with those of adducts **1–4** shows a decrease in the *s*-electron density without change in the tin *p*-population symmetry. This does not indicate that the same *p*-electron symmetry is present on tin in $[SnX_6]^{2-}$ and in **1–4**, but rather that the relatively large natural linewidth of ^{119m}Sn [19] does not allow the detection of the small *p*-orbital asymmetries which certainly exist in **1–4**.

Within the well known limits of the point-charge model [16], a non-zero electric quadrupole interaction is calculated (Table 2), assuming a regular *cis*-octahedral geometry for **1–4**. The calculated splittings imply a minor anisotropy among the σ-bonding orbitals and then a small principal component of the electric field gradient tensor (V_{zz}) along the X–Sn–X axis. The imbalance in electron density would arise from small differences in the tin *p*-electron involvement in the Sn–X and Sn–N bonds. The calculated V_{zz} for the adducts **1–3** is positive; this results in a negative QS because the ^{119m}Sn nuclear quadrupole moment is negative. A positive V_{zz} implies that more negative charge is present in the equally populated orbitals p_x and p_y than in the apical bonds Sn–X, implying different Sn–X bond lengths in **1–4**, while an equal bond length is expected in $[SnX_6]^{2-}$ (X = Cl, Br, or I) [20].

The Mössbauer spectrum of the adduct $SnBr_3(OH)(L'\text{-}L')$ (**5**) containing one OH group in place of Br (obtained probably because of the presence of traces of moisture during its preparation) is shown in Fig. 1. Because of the presence of the OH group, which is not sterically equivalent to Br although a monoanion, the spectrum shows two Mössbauer components (Table 2) attributed to the two octahedral geometrical isomers, *trans*-N, OH (unsplit line) and *trans*-Br, OH (split line). These components are in the ratio of about 2:1 as calculated from the peak

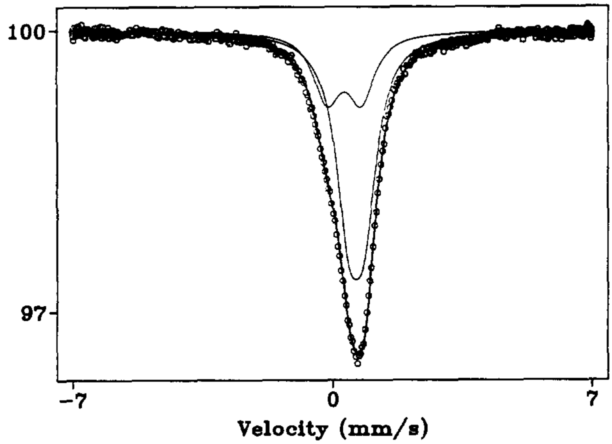

Fig. 1. Mössbauer spectrum of $SnBr_3(OH)(L'\text{-}L')$ (**5**) at 4.2 K (experimental points shown by circles, continuous lines show the fitted curve and the deconvoluted components).

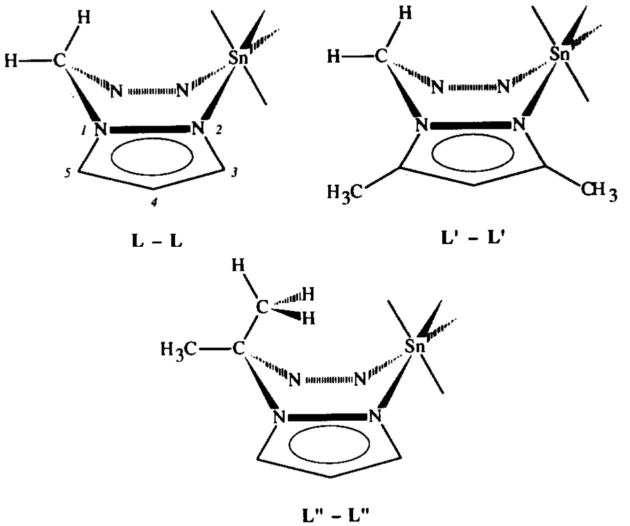

Fig. 2. Octahedral coordination around tin for the three ligands.

areas (Table 1). The alternative possibilities of trigonal bipyramidal geometry with ionic OH^- and bidentate L′–L′, or bound hydroxide and unidentate L′–L′ are excluded on the basis of point-charge model.

The Mössbauer parameters of **1–4** indicate that even if L′–L′ is a slightly more hindered ligand than L–L, its presence does not seem to perturb the tin coordination environment. The *s*-electron density at the tin nucleus is indeed insensitive to the nature of L–L or L′–L′, indicating that there is no steric inhibition to octahedral geometry to accommodate these ligands even if L′–L′ contains a 3-methyl group which points towards the tin but between the other tin-bonded groups.

The presence of the ligand L″–L″, as shown in Fig. 2, might provoke steric interactions from the flag-pole position in the boat conformation (the only one possible for such polypyrazolyl complexes) and might introduce substantial deviations in the octahedral coordination geometry.

The unsplit Mössbauer line obtained from $SnCl_4$(L″–L″)H_2O (**6**) indicates the presence of the same *cis*-octahedral geometry deduced for **1–4**. In addition, the *s*-electron density, which is practically the same for **1**, **2** and **6**, suggests a similarity of the stereochemistry at the tin site for all these chloro-derivatives. The alternative possibility for **6**, of a trigonal bipyramidal geometry with unidentate L″–L″ and with uncoordinated water is ruled out because measurable splittings are predicted for the two possible isomers. The octahedral isomers with unidentate L″–L″ and coordinated water are excluded for the same reason.

The isomer shifts of the adducts **7–10**, varying from 0.78 to 0.92 mm/s, compare well with literature values of monoalkyltin(IV) halides [15]. For $RSnX_3$(L–L)-type adducts, two geometric isomers (*trans*-RN and -RX) are possible in the octahedral geometry, and their calculated splittings are reported in Table 2. The *trans*-RN geometry for the adducts **7–9** and a *trans*-RX geometry for $PhSnCl_3$(L″–L″) (**10**) are consistent with the point-charge model. Calculations considering L–L, L′–L′ and L″–L″ to be unidentate are not consistent with the observed values.

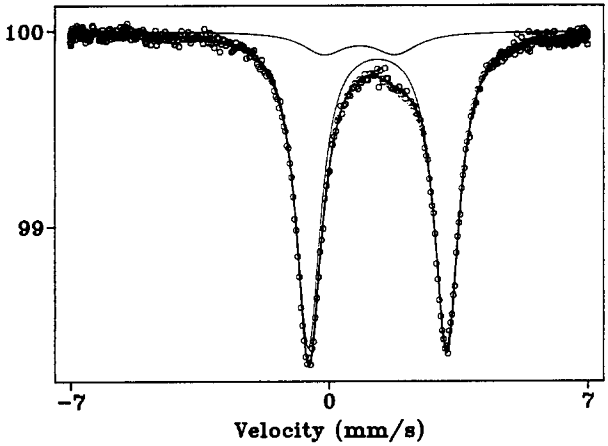

Fig. 3. Mössbauer spectrum of $Ph_2SnCl_2(L\text{–}L)$ (**12**) at 4.2 K (experimental points shown by circles, continuous lines show the fitted curve and the deconvoluted components).

The Mössbauer parameters of **7** and **8** show that the introduction of methyls into the pyrazole ring increases both the *s*-electron density and the asymmetry in the *p*-population with possible distortions in the *trans*-RN octahedral geometry. The Mössbauer parameters of **9** and **10** show that the introduction of methyls in the bridging methylene does not affect the *s*-electron density but decreases the quadrupole splitting by about 0.3 mm/s. This suggests that, because of steric effects induced by the L″–L″ ligand, a structural change takes place which determines a transition from the *trans*-RN (**9**) to the *trans*-RX (**10**) octahedral geometry. On comparing the Mössbauer parameters of **7–10** with those of the inorganic adducts **1**, **2** and **6**, it is clear that the steric hindrance of L″–L″ is a critical parameter in monoalkyltin(IV)derivatives **7–10**. This is also reflected in the lower reactivity of the ligand L″–L″ found for all the starting tin(IV) halides and especially with diorganotin(IV) halides [1b], which do not form adducts in the same preparative conditions; this is probably a consequence not only of the additional steric requirement, but also of the poorer Lewis acidity of diorganotin(IV) halides.

The proton NMR spectra of **11, 12** indicate that the boat conformation of the ligands bound to the metal centre [5] undergoes a rapid inversion process, and that these adducts are present in solution as sets of three fast equilibrating octahedral geometrical isomers: *trans*-NX, -XX and -RR.

The Mössbauer spectra of **11**, **13** and **14** consist of a single quadrupole doublet, whereas **12** shows two doublets (Fig. 3). Both isomer shifts [15] and calculated splittings in Table 2 point to the presence of the octahedral isomers *trans*-RR and *trans*-NX. On the basis of the Mössbauer resonance area, the two isomers are in the ratio of about 9:1. For the *trans*-RR isomers of **11, 12, 13** and **14**, the octahedral geometries are predicted by the point-charge model to be distorted, with C–Sn–C bond angles of 169°, 167°, 167° and 170°, respectively. For the *trans*-NX isomer **12** it is 97°. The possible trigonal bipyramidal geometries are ruled out because their splittings would be too small.

Osmometric measurements and conductivity values point to an extensive ionic dissociation of the adducts in solution [1]. On the other hand, the compounds have relatively low melting points and the Lamb–Mössbauer factor is too small to observe the Mössbauer effect at room temperature; this implies a rapid decrease in the strength of the intermolecular bonds with increasing temperature and may indicate a discrete molecular structure. In addition, the structural assignments on the basis of the point-charge model (Table 2) imply a monomeric structure.

Additional support for a discrete molecular structure of the R_2SnCl_2(L–L)-type adducts is provided by the X-ray structures of *trans*- and *cis*-[Sn(ClC_6H_4)$_2$$Cl_2$(4,4'-$Me_2$bipy)] and of *cis*-[Sn($C_6H_4Cl_4$)$_2$$Cl_2$(4,4'-$Me_2$bipy)] containing non-bridging bidentate bipyridine derivatives [21,22].

In conclusion, even if the stereochemistry is the result of a fine balance between electronic and steric effects, a more or less distorted octahedral coordination is always present in the adducts of Table 1. The bis(pyrazol-1-yl)methane-type ligands are bidentate, not bridging, and of a similar electron-donor power, comparable to that of 2,2'-bipyridine. The accommodation of L–L or L'–L' ligand in an octahedral geometry does not present steric problems. However, the accommodation of L"–L", easy in SnX_4(L"–L"), presents steric problems in the monoalkyltin adducts and is impossible for dialkyltin(IV) compounds.

Experimental

The compounds of Table 1 were prepared as described in [1]. Their identity and purity were checked by elemental analysis, m.p. determinations, and comparison of the IR, ^1H and ^{13}C NMR spectra with those already reported.

The $Ca^{119m}SnO_3$ Mössbauer source and the absorbers, with a ^{119}Sn content of about 0.20 mg/cm^2, were both kept at 4.2 K. A sinusoidal velocity waveform and an intrinsic germanium detector were used. The fitting procedure was performed by Grosse's program, MOS 90.

A minor component, probably due to decomposition, and attributable to tin(II) is present in the Mössbauer spectrum of **8** and **11**. A minor component attributed to tetrahedral tin(IV) is present in **10**. Present and literature data have been compared without SOD shift correction.

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