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Synthesis and Spectroscopic Characterization of Tin(II) and Tin(IV) Complexes Containing 2,3,5,6-Tetrakis(α-pyridyl)pyrazine as a Bridging Ligand[#]

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Neste trabalho foram investigadas as reações entre o ligante heterocíclico nitrogenado 2,3,5,6-tetraquis(α-piridil)pirazina, TPP, e seis precursores de estanho, a saber: $SnCl_2$, SnX_4 (X = Cl ou Br), $SnRCl_3$ (R = Ph ou Me) e $SnPh_2Cl_2$. Os produtos foram caracterizados por microanálise (C, H, N e Sn), espectroscopia no infravermelho (4000-200 cm^{-1}), RMN de ^1H, $^{13}C\{^1H\}$, ^{13}C-CP/MAS, ^{119}Sn e ^{119}Sn-MAS, bem como por espectroscopia Mössbauer de ^{119}Sn. Todas as reações levaram ao isolamento de complexos bimetálicos, nos quais o TPP se comportou como um ligante bis-bidentado em ponte, ligando-se a cada centro metálico através de dois átomos de nitrogênio piridínicos. Este modo de coordenação é ainda raro na literatura e, pela primeira vez, é observado em complexos de TPP com um metal representativo.

In this work we investigated the reactivity of the nitrogen heterocyclic ligand 2,3,5,6-tetrakis(α-pyridyl)pyrazine, TPP, towards six tin-containing reagents, namely $SnCl_2$, SnX_4 (X = Cl or Br), $SnRCl_3$ (R = Ph or Me), and $SnPh_2Cl_2$. The products were characterized by microanalysis (C, H, N, and Sn), IR spectroscopy (4000-200 cm^{-1}), ^1H, $^{13}C\{^1H\}$, ^{13}C-CP/MAS, ^{119}Sn, and ^{119}Sn-MAS NMR spectroscopy, as well as by ^{119}Sn Mössbauer spectroscopy. All reactions yielded bimetallic adducts, in which TPP behaved as a bis-bidentate bridging ligand, binding to each metallic center through two pyridine nitrogen atoms. This coordination mode is so far quite rare and, for the first time, is reported for main group metal-TPP complexes.

Keywords: Sn(II), Sn(IV), bimetallic complexes, 2,3,5,6-tetrakis(α-pyridyl)pyrazine

Introduction

2,3,5,6-tetrakis(α-pyridyl)pyrazine, TPP, is a versatile ambidentate ligand containing six Lewis-basic nitrogen sites and at least seven different coordination modes with transition metals.[1-16] The seven chelating modes hitherto encountered for TPP are illustrated in Figure 1. The reactivity of this ligand towards transition metal species has attracted considerable attention over the past twenty years.[1-16] However, studies of reactions between TPP and main group metal compounds are absent in the literature. Owing to this paucity of information, we decided to investigate the reactivity and coordinating behavior of

TPP towards Sn(II) and Sn(IV) compounds, namely $SnCl_2$, SnX_4 (X = Cl or Br), $SnRCl_3$ (R = Ph or Me), and $SnPh_2Cl_2$. The various complexes thus produced were characterized by a number of different spectroscopic methods.

The coordination chemistry of tin, particularly that of organotin compounds, is quite rich.[17-19] However, this work shows that the stannylated products described herein are all bimetallic adducts and exhibit a similarity of structural behavior. Regardless of the stannylated reagent, TPP coordinates each tin atom through two pyridine nitrogen atoms, in the bis-bidentate 1 chelating mode (Figure 1). This sort of TPP coordination mode was first reported for the cationic part of the salt {[Pt(PEt$_3$)Cl]$_2$-μ-TPP}[Pt(PEt$_3$)(SnCl$_3$)$_4$][12] and is reproduced in the present study.
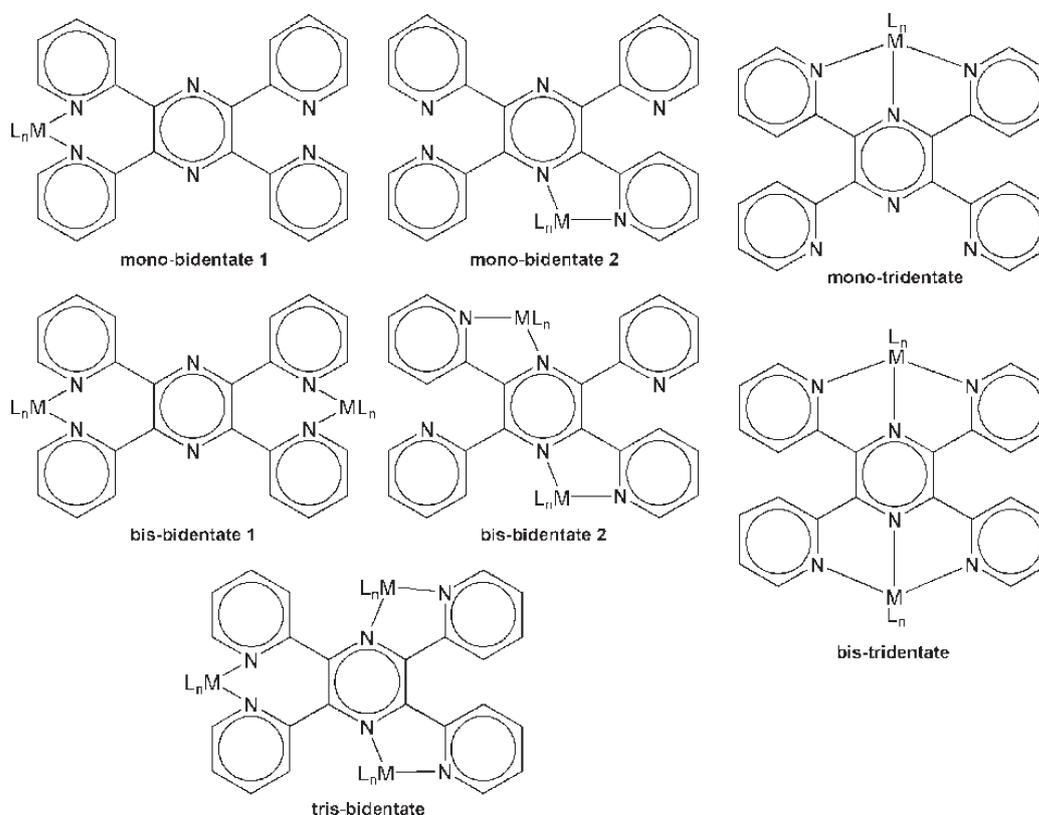
Figure 1. The seven coordination modes reported for 2,3,5,6-tetrakis(α-pyridyl)pyrazine.

Experimental

General procedures

All reactions were carried out under an Ar or N_2 atmosphere using Schlenk glassware and vacuum/inert-gas line manipulation techniques. Solvents were dried by standard procedures and distilled immediately prior to use. 2,3,5,6-tetrakis(α-pyridyl)pyrazine (TPP) was synthesized according to Goodwin & Lions's method.[20] All other chemicals were obtained from commercial sources (Strem or Aldrich) and used as received.

Physical measurements

Decomposition points were determined on a Mel-Temp II (Lab. Devices, Inc.) apparatus. Elemental analyses (C, H, and N) were conducted on a Perkin-Elmer 2400 CHN Elemental Analyzer. Tin was analyzed on a Hitachi Z-8200 atomic absorption spectrophotometer. IR spectra were recorded either on a 283B Perkin-Elmer or on a Magna-IR760 FTIR Nicolet spectrometer. The IR spectra were obtained in the 4000-200 cm^{-1} range using CsI pellets. ^{1}H and $^{13}C\{^1H\}$ NMR spectra in solution were acquired from a Bruker DRX200 instrument operating at 200.00 and 50.30 MHz, respectively. The solution ^{119}Sn NMR spectra

were obtained from a Bruker DRX400 spectrometer operating at 149.17 MHz. Both ^{13}C-CP/MAS and ^{119}Sn-MAS spectra were recorded on a Bruker DRX300 spectrometer operating at 75.47 and 111.92 MHz, respectively. In order to obtain the isotropic chemical shift values, the sample was spun at 6 and 7.5 kHz in the ^{13}C-CP/MAS spectra and also at 8 kHz in the ^{119}Sn-MAS spectra. All NMR studies were performed at room temperature, and the chemical shift values were determined in relation to $SiMe_4$ for the ^{1}H and ^{13}C nuclei and to an external reference of $SnMe_4$ for the ^{119}Sn nucleus. ^{119}Sn Mössbauer spectra were obtained from a constant acceleration spectrometer moving a $CaSnO_3$ source at room temperature. The samples were analyzed at liquid N_2 temperature, and the isomer shift values are given with respect to that source. All Mössbauer spectra were computer-fitted assuming Lorentzian lineshapes.

Synthesis of $[(SnCl_4)_2$-μ-TPP] (**1**) and $[(SnBr_4)_2$-μ-TPP](**2**)

A solution of SnX_4 (X = Cl: 0.20 mL, 0.46 g, 1.76 mmol; X = Br: 0.23 mL, 0.77 g, 1.76 mmol) was added under constant magnetic stirring to a suspension of TPP (0.34 g, 0.88 mmol) in EtOH (35 mL). When X = Cl, **1** immediately precipitated as a white solid. When X = Br, the resulting solution was refluxed for 2h and cooled to room

temperature, leading to the formation of **2** as a yellow powder. Both **1** and **2** were filtered off, washed with EtOH and Et$_2$O, and dried under vacuum. The products were recrystallized from a 1:1 mixture of EtOH and MeCN, yielding 0.60 g of **1** (75%) and 0.69 g of **2** (63%).

Data for **1**. mp: 283 ^{o}C (dec.). Anal. Calc. for C$_{24}$H$_{16}$N$_6$Cl$_8$Sn$_2$: C, 31.7; H, 1.8; N, 9.2; Sn, 26.1%. Found: C, 32.4; H, 1.7; N, 9.1; Sn, 26.2%. IR ν_{max}/cm^{-1}: ν(CH), 3060 (m); ν(CC/CN), 1594 (s), 1570 (s), 1485 (s), 1390 (s); δ(CH), 771 (s), 740 (s); ν(Sn-N), 409 (w); ν(Sn-Cl), 279 (s). ^{1}H NMR (DMF-d_7), δ (ppm): 8.57 (4H, m, H6); 8.36-8.24 (8H, m, H3, H4); 7.96 (4H, m, H5). ^{13}C{^{1}H} NMR (DMF-d_7), δ (ppm): 157.3 (C2, pyrazine ring); 154.2 (C2); 151.8 (C6); 143.5 (C3); 139.2 (C4); 130.3 (C5).

Data for **2**. mp: 257 ^{o}C (dec). Anal. Calc. for C$_{24}$H$_{16}$N$_6$Br$_8$Sn$_2$: C, 22.8; H, 1.3; N, 6.6; Sn, 18.8%. Found: C, 23.4; H, 1.4; N, 6.8; Sn, 19.5%. IR ν_{max}/cm^{-1}: ν(CH), 3064 (m); ν(CC/CN), 1590 (s), 1573 (s), 1489 (s), 1393 (s); δ(CH), 778 (s), 745 (s); ν(Sn-N), 394 (w). ^{1}H NMR (CD$_3$CN), δ (ppm): 8.54 (4H, m, H6); 8.38-8.27 (8H, m, H3, H4); 7.91 (4H, m, H5). ^{13}C{^{1}H} NMR (CD$_3$CN), δ (ppm): 156.2 (C2, pyrazine ring); 152.7 (C2); 151.4 (C6); 142.3 (C3); 140.8 (C4); 131.6 (C5).

Synthesis of [(SnPhCl$_3$)$_2$-µ-TPP] (3), [(SnMeCl$_3$)$_2$-µ-TPP] (4), and [(SnPh$_2$Cl$_2$)$_2$-µ-TPP] (5)

To a suspension of TPP (0.15 g, 0.39 mmol) in EtOH (30 mL), the appropriate organotin chloride, SnR$_{4-n}$Cl$_n$ (n = 3, R = Ph: 0.13 mL, 0.24 g, 0.78 mmol; n = 3, R = Me: 0.19 g, 0.78 mmol; n = 2, R = Ph: 0.27 g, 0.78 mmol), was added under vigorous magnetic stirring. Each reaction mixture was kept under reflux for 6h, and then, reduction of the volume to 2 mL was performed. The precipitation of the products was induced by addition of a 2:1 mixture of THF:hexane. The products were separated by filtration, washed with EtOH and Et$_2$O, and dried under vacuum. The isolated complexes were recrystallized from a 1:1:2 mixture of DMF:hexane:EtOH, yielding 0.23 g of **3** (60%), 0.21 g of **4** (61%), and 0.24 g of **5** (58%).

Data for **3**. mp: 270 ^{o}C (dec). Anal. Calc. for C$_{36}$H$_{26}$N$_6$Cl$_6$Sn$_2$: C, 43.6; H, 2.6; N, 8.5; Sn, 23.9%. Found: C, 44.3; H, 2.7; N, 8.9; Sn, 24.3%. IR ν_{max}/cm^{-1}: ν(CH), 3085 (m), 3068 (m); ν(CC/CN), 1610 (s), 1576 (s), 1490 (s), 1450 (s); δ(CH), 772 (s), 730 (s); ν(Sn-N), 410 (w); ν(Sn-Cl), 270 (s). ^{1}H NMR (DMF-d_7), δ (ppm): 8.51 (4H, m, H6); 8.38-8.25 (8H, m, H3, H4); 7.95 (4H, m, H5); 7.89 (4H, m, H$_o$, Ph); 7.55-7.47 (6H, m, H$_m$, H$_p$, Ph). ^{13}C{^{1}H} NMR (DMF-d_7), δ (ppm): 157.1 (C2, pyrazine ring); 154.5 (C2); 152.3 (C6); 143.8 (C3); 140.6 (C4) 130.8 (C5); 142.6 (C$_{ipso}$); 134.8 (C$_o$); 131.3 (C$_p$); 128.1 (C$_m$).

Data for **4**. mp: 256 ^{o}C (dec). Anal. Calc. for C$_{26}$H$_{22}$N$_6$Cl$_6$Sn$_2$: C, 35.9; H, 2.6; N, 9.7; Sn, 27.3%. Found: C, 37.7; H, 2.8; N, 10.2; Sn, 27.0%. IR ν_{max}/cm^{-1}: ν(CH), 3060 (m), 2913 (m); ν(CC/CN), 1599 (s), 1572 (s), 1486 (s), 1380 (s); δ(CH), 776 (s), 739 (s); ν(Sn-N), 408 (w); ν(Sn-Cl), 273 (s). ^{1}H NMR (CD$_3$CN), δ (ppm): 8.53 (4H, m, H6); 8.34-8.21 (8H, m, H3, H4); 7.92 (4H, m, H5); 1.27 (6H, Me). ^{13}C{^{1}H} NMR (CD$_3$CN), δ (ppm): 156.5 (C2, pyrazine ring); 153.3 (C2); 152.4 (C6); 142.7 (C3); 141.3 (C4); 130.6 (C5); 28.7 (Me).

Data for **5**. mp: 210 ^{o}C (dec). Anal. Calc. for C$_{48}$H$_{36}$N$_6$Cl$_4$Sn$_2$: C, 53.6; H, 3.4; N, 7.8; Sn, 22.1%. Found: C, 51.9; H, 3.1; N, 7.6; Sn, 21.6%. IR ν_{max}/cm^{-1}: ν(CH), 3080 (m), 3061 (m); ν(CC/CN), 1596 (s), 1576 (s), 1478 (s), 1400 (s); δ(CH), 796 (s), 732 (s), 719 (s); ν(Sn-N), 402 (w); ν(Sn-Cl), 270 (s). ^{1}H NMR (CD$_3$CN), δ (ppm): 8.50 (4H, m, H6); 8.43-8.29 (8H, m, H3, H4); 7.93 (4H, m, H5); 7.85 (8H, m, H$_o$, Ph); 7.57-7.45 (12H, m, H$_m$, H$_p$, Ph). ^{13}C{^{1}H} NMR (CD$_3$CN), δ (ppm): 155.1 (C2, pyrazine ring); 153.1 (C2); 152.5 (C6); 144.6 (C3); 140.1 (C4); 129.5 (C5); 141.2 (C$_{ipso}$); 135.5 (C$_o$); 132.7 (C$_p$); 127.6 (C$_m$).

Synthesis of [(SnCl$_2$)$_2$-µ-TPP] (6)

Solid TPP (0.36 g, 0.93 mmol) was added under vigorous magnetic stirring to a solution of anhydrous SnCl$_2$ (0.41 g, 2.17 mmol) in EtOH (25 mL). A yellow solid immediately precipitated. The reaction mixture was kept under stirring for two additional days at room temperature. The yellow solid was then isolated by filtration, washed with EtOH and MeOH, and dried under vacuum. After drying, product **6** became orange and was stored under argon. The yield of **6** was 0.50 g (70%).

Data for **6**. mp: 190 ^{o}C (dec). Anal. Calc. for C$_{24}$H$_{16}$N$_6$Cl$_4$Sn$_2$: C, 37.6; H, 2.1; N, 11.0; Sn, 30.9%. Found: C, 39.6; H, 1.7; N, 11.2; Sn, 30.7%. IR ν_{max}/cm^{-1}: ν(CH), 3074 (w), 3031 (w); ν(CC/CN), 1592 (s), 1569 (w), 1525 (w), 1482 (m), 1446 (m), 1397 (vs); δ(CH), 797 (m), 747 (m); ν(Sn-N), 456 (w), 416 (m); ν(Sn-Cl), 253 (s), 229 (m). ^{1}H NMR (CD$_3$CN), δ (ppm): 8.47 (4H, d, J_{HH} = 4.5 Hz, H6); 8.05-7.96 (8H, m, H3, H4); 7.59 (4H, m, H5). ^{13}C-CP/MAS, δ (ppm): C2-pyrazine ring: not observable; 150.3 (C2); 147.9 (C6); 143.7 (C3); 140.6 (C4); 128.0 (C5). Due to the low solubility of **6** in commom deuterated solvents and decomposition in DMF-d_7 and DMSO-d_6, its solution ^{13}C{^{1}H} and ^{119}Sn NMR spectra could not be measured.

Because of their importance for the present study, the ^{119}Sn NMR and Mössbauer spectroscopic data are separately listed in Table 1.

Table 1. ^{119}Sn NMR and Mössbauer spectral data

Compound	^{119}Sn NMR δ (ppm)	[119]Sn Mössbauer δ (mm s^{-1})	ΔE_Q (mm s^{-1})
SnCl$_4$	-150[a, 21]	0.85[21]	0.00
	-601[b, 22]		
SnBr$_4$	-638[c, 21]	1.15[21]	0.00
SnCl$_2$	-358[d, 21]	4.06(2)[24]	0.66(4)
CsSnCl$_3$	-30[e, 21]	3.40[25]	1.22
SnPhCl$_3$	-63[f, 23]	1.10[26]	1.80
SnMeCl$_3$	+20[g, 23]	1.20[27]	1.99
SnPh$_2$Cl$_2$	-32[f, 23]	1.40[26]	2.80
(**1**)	-631[h]	0.49(1)	0.32(2)
(**2**)	-485[i]	0.81(1)	0.38(2)
(**3**)	-675[h]	0.68(1)	2.10(2)
(**4**)	-610[i]	0.79(1)	2.08(2)
(**5**)	-640[i]	1.23(1)	3.45(1)
(**6**)	-584[j]	3.44(5)	1.14(6)

[a] neat; [b] in MeOH; [c] in CS$_2$; [d] in DMSO; [e] in CH$_2$Cl$_2$/C$_6$D$_6$; [f] in CD$_2$Cl$_2$; [g] in CDCl$_3$; [h] in DMF-d_7; [i] in CD$_3$CN; [j] solid state.

Results and Discussion

Elemental analyses agree with the supposition that all products are bimetallic adducts of general formula [(SnL$_n$)$_2$TPP], in which SnL$_n$ stands for the different stannylated precursors. The analytical and spectroscopic data point to the fact that complexes **1** to **5** have two hexacoordinate Sn(IV) sites, whereas complex **6** has two tetracoordinate Sn(II) centers.

In the IR spectra, the ν(CC/CN) bands were shifted from 1590-1390 cm^{-1} in free TPP to higher wavenumbers in the products. Additionally, new ν(Sn-N) bands appeared in the low-frequency region of the spectra, as expected. Moreover, the ν(Sn-X) (X = Cl or Br) bands were shifted to lower wavenumber values in relation to the free stannylated reagents.

The coordination of TPP is also indicated by the ^{1}H and [13]C{[1]H} (or ^{13}C-CP/MAS in the case of **6**) NMR data. With no exception, the NMR signals assigned to the H and C atoms of TPP in the products moved to higher δ values with respect to those of the free ligand. Moreover, the number and integration of the ^{1}H signals imply that there are no uncoordinated pyridine rings in **1** to **6**, suggesting that TPP may be symmetrically attached to both metallic centers in each adduct. Thus, on the basis of the ^{1}H and ^{13}C NMR spectra, only the bis-bidentate 1 or bis-tridentate chelating modes (Figure 1) can occur in **1** to **6**.

Table 1 shows the ^{119}Sn NMR and [119]Sn Mössbauer spectral data collected for the products and for other tin compounds. Our six adducts exhibit only one sharp ^{119}Sn NMR signal. This indicates that both tin atoms in each bimetallic product are chemically and magnetically equivalent in the NMR time scale. Except for **2**, the [119]Sn

chemical shift values, δ([119]Sn), for the products are significantly lower than those for their precursors. An important feature of [119]Sn chemical shifts is that an increase in coordination number normally leads to lower values of δ([119]Sn) due to shielding effects.[19] This shift upon complexation has been repeatedly shown in work by this group and by others.[23,28-31] If one takes SnCl$_4$, its values of δ([119]Sn) are -150 and -601 ppm as the neat compound and in its MeOH solution, respectively (Table 1). This difference suggests that in MeOH the metal is hexacoordinate due to solvation. In fact, the value of δ([119]Sn) observed for SnCl$_4$ in MeOH is analogous to that measured for **1** (Table 1). A more striking case arises when one compares **1** with [SnCl$_4$(DPS)][31] (DPS = di(2-pyridyl)sulfide), in which δ([119]Sn) is -636 ppm in DMF-d_7 and the ligand DPS forms an N,N-bonded chelate. The similarity between the δ([119]Sn) values for both [(SnCl$_4$)$_2$-μ-TPP] and [SnCl$_4$(DPS)] suggests that in the former each Sn(IV) center is hexacoordinate and thus, TPP binds to each stannylated site through two pyridine nitrogen atoms, according to the bis-bidentate 1 coordination mode (Figure 1). The same interpretation can be made by comparing δ([119]Sn) of **2** (-485 ppm) with that of [SnBr$_4$(DPS)] (-502 ppm).[31] Curiously, the value of δ([119]Sn) of SnBr$_4$ (Table 1) is lower than that measured for **2**. It has been pointed out that, for adducts obtained from SnBr$_4$, there appears to be no obvious relationship between the coordination number of tin and the value of δ([119]Sn).[28] In **3** to **5** the upfield shift in the values of δ([119]Sn) (Table 1), in relation to their precursors, also suggests the formation of hexacoordinate Sn(IV) compounds.

Summing up the discussion in terms of the NMR results, of the seven coordinating possibilities so far reported for TPP (Figure 1), only the symmetrical bis-bidentate 1 and bis-tridentate are possible for **1** to **6**. Both afford equivalent tin centers; nevertheless, the former leads to hexacoordinate Sn(IV) and tetracoordinate Sn(II) centers, whereas the latter leads to heptacoordinate Sn(IV) and pentacoordinate Sn(II) products. Heptacoordinate Sn(IV) complexes, however, have much lower [119]Sn chemical shifts than those obtained for **1** to **5**.[30,32] Therefore, the ^{119}Sn NMR results point to hexacoordinate tin centers in the Sn(IV) products. With respect to complex **6**, since only a few data about ^{119}Sn-MAS NMR spectra of Sn(II) compounds are available for comparison with our result, a discussion concerning the coordination mode of TPP in **6** will be centered on its [119]Sn Mössbauer spectrum. In turn, the [119]Sn Mössbauer data of the Sn(IV) adducts corroborate the conclusions from the ^{119}Sn NMR spectra. This shows that TPP acts as a bis-bidentate 1 ligand in both solution and the solid state and leads to the conclusion that no dissociation of complexes **1** to **5** in coordinating solvents (DMF-d_7 or CD$_3$CN) occurred.

Table 1 gives the [119]Sn Mössbauer parameters for the precursors and products. Both isomer shifts (δ) and quadrupole splittings (ΔE_Q) show great variation upon complexation. Invariably, the isomer shift values of **1** to **6** are lower than those of their precursors. Furthermore, the presence of only one doublet in the [119]Sn Mössbauer spectra also indicates the existence of just one type of tin atom in each dinuclear adduct.

[119]Sn Mössbauer δ values are directly dependent upon the 5s-electron density at the Sn nucleus.[17-19,21] Thus, an increase in the coordination number of tin leads to a decrease in the δ value. [119]Sn Mössbauer spectroscopy can also be reliably used to distinguish between the 2+ and 4+ oxidation states of tin. Usually, δ values in the interval from -0.5 to 2.1 mm s^{-1} are expected for Sn(IV) compounds, and Sn(II) complexes present δ values ranging from +2.5 to 5.0 mm s^{-1}.[21] Based on this, our Mössbauer data are consistent with the presence of Sn(IV) sites in complexes **1** to **5** and Sn(II) centers in **6**. ΔE_Q parameters relate to a change in the symmetry of electron density distribution around the Sn nucleus.[17-19,21] The three inorganic precursors have ΔE_Q values of zero (SnCl$_4$ and SnBr$_4$) or very low (SnCl$_2$). After complexation, the ΔE_Q values of **1**, **2**, and **6** became higher than those of their precursors, showing an increase in electron density asymmetry around the Sn centers. A similar increase in ΔE_Q values also takes place upon coordination of the three organotin reagents.

In all the Sn(IV) complexes the 5s-electron density at tin was reduced from about 25% (sp^3 hybrid) in the precursors to *ca.* 17% (sp^3d^2 hybrid, supposing hexacoordinate tin) in the complexes, entailing a reduction in the δ values. Regarding the actual isomer shifts, it is interesting to draw attention to the change observed when one compares SnCl$_4$ (0.85 mm s^{-1}) with [SnCl$_4$(DPS)] (0.48 mm s^{-1})[31] and [(SnCl$_4$)$_2$-μ-TPP] (0.49 mm s^{-1}). Also, a similar change is verified comparing SnBr$_4$ (1.15 mm s^{-1}) with [SnBr$_4$(DPS)] (0.74 mm s^{-1})[31] and [(SnBr$_4$)$_2$-μ-TPP] (0.81 mm s^{-1}). These results indicate not only an increase in the coordination number of tin, from four to six, in **1** and **2**, but also similar coordinating environments around tin in the DPS and TPP complexes of SnCl$_4$ and SnBr$_4$. Other analogies arise when one takes the δ values of [(SnPhCl$_3$)$_2$-μ-TPP] (0.68 mm s^{-1}) and [SnPhCl$_3$(bipy)] (bipy = 2,2'-bipyridine) (0.87 mm s^{-1}),[33] [(SnMeCl$_3$)$_2$-μ-TPP] (0.79 mm s^{-1}) and [SnBuCl$_3$(bipy)] (0.87 mm s^{-1}),[33] as well as the δ values of [(SnPh$_2$Cl$_2$)$_2$-μ-TPP] (1.23 mm s^{-1}), [SnPh$_2$Cl$_2$(bipy)] (1.22 mm s^{-1}),[26] and [SnPh$_2$Cl$_2$(bipym)] (bipym = 2,2'-bipyrimidine) (1.23 mm s^{-1}).[34] Insofar as [SnPhCl$_3$(bipy)], [SnBuCl$_3$(bipy)], [SnPh$_2$Cl$_2$(bipy)], and [SnPh$_2$Cl$_2$(bipym)] have hexacoordinate tin atoms attached to pyridine (or pyrimidine) nitrogen atoms, **3**, **4**, and **5**

should also be hexacoordinate and in these complexes the tin atoms should be coordinated to the pyridine nitrogen atoms of TPP. In the bipym complex [SnPh$_2$Cl$_2$(bipym)] the value of ΔE_Q is 3.43 mm s^{-1}, and its X-ray structure shows that the two Ph groups are *trans* to each other.[34] In [(SnPh$_2$Cl$_2$)$_2$-μ-TPP], **5**, ΔE_Q = 3.45 mm s^{-1}. This proximity in the values of ΔE_Q suggests similar geometries for both complexes, thereby pointing that in **5** the two Ph groups must also be *trans* to each other. Indeed, ΔE_Q can be used as a powerful tool for the assignment of structures of *cis* and *trans* diorganotin compounds of the SnR$_2$Cl$_2$(LL) type, in which LL stands for a bidentate ligand.[19] It is expected, therefore, that *trans* complexes show ΔE_Q values of about 4.0 mm s^{-1}, whereas *cis* isomers exhibit ΔE_Q values twice as smaller. Our conclusion is that **5** is likely to have the two Ph groups *trans* to each other.

In solid anhydrous tin(II) chloride, the tin atom is surrounded by nine chlorine atoms, leading to a facially capped trigonal prismatic arrangement.[21,35] Of the nine Sn-Cl distances in solid SnCl$_2$, three are very short and the others are longer and of variable length. In view of this, it is not possible to clearly state the coordination number of tin in solid SnCl$_2$. Thus, it is difficult to discuss the coordination number of tin in **6** solely from a comparison between its Mössbauer parameters and those of SnCl$_2$. On the other hand, in the related compound [SnCl$_2$(pyridine)$_2$] δ is 3.02 mm s^{-1}.[36] The δ value of **6**, 3.44 mm s^{-1}, is very similar to that of [SnCl$_2$(pyridine)$_2$], suggesting similar tin environments in both complexes. Thus, we propose that in **6** TPP also coordinates each stannylated center at two pyridine nitrogen atoms, according to the bis-bidentate 1 chelating mode.

It is important to mention that the bis-bidentate 1, as well as the mono-bidentate 1 chelating modes of TPP do not lead to planar metallacycles, as Figure 1 might suggest. In fact, due to rotation about the single bonds uniting the pyridine rings and the central pyrazine ring, the adjacent pyridine rings of TPP acquire a non-planar configuration upon coordination through the mono- or bis-bidentate 1 bonding modes.[12,13]

Conclusions

The present work describes an unprecedented case of the reactivity of TPP towards several inorganic and organometallic stannylated species. Six different adducts were prepared, and all of them are bimetallic species, with TPP bridging two tin centers. From spectroscopic data we conclude that TPP coordinates both Sn(IV) and Sn(II) centers in the same mode, namely the rare bis-bidentate 1 chelating mode.

Acknowledgements

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