Article

Synthesis, Structural and Spectral Studies of Five- and Six-Coordinate Adducts of Organotin(IV) Halides Containing Dibenzylsulfoxide (dbso) as Ligand. The Crystal Structures of *fac*-[MeSnCl$_3$(dbso)$_2$] and *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$]

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A reação do ligante ambidentado dibenzilsulfóxido (dbso) com Me$_2$SnCl$_2$ na proporção molar 1:1 leva à formação do produto pentacoordenado [Me$_2$SnCl$_2$(dbso)], enquanto Ph$_2$SnCl$_2$ leva à formação do complexo hexacoordenado *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$], utilizando as mesmas condições de reação. Por outro lado, a reação com ^{n}Bu$_2$SnCl$_2$ forma o produto bimetálico [{^{n}Bu$_2$SnCl$_2$(dbso)}$_2$], o qual provavelmente possui núcleos de estanho(IV) octaédricos e cloretos em ponte. Os complexos [MeSnCl$_3$(dbso)$_2$] e [Ph$_3$SnCl(dbso)] também foram preparados. Todos os produtos foram estudados por análise elementar e por espectroscopias no IV, RMN (^{1}H, ^{13}C, ^{119}Sn) e Mössbauer. As espécies hexacoordenadas *fac*-[MeSnCl$_3$(dbso)$_2$] e *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$] foram também estudadas por difratometria de raios X; as determinações estruturais revelaram que estes compostos cristalizam-se nos sistemas cristalinos ortorrômbico, *Pbcn*, e monoclínico, *P2$_1$/c*, respectivamente. As moléculas possuem átomos de estanho(IV) numa geometria octaédrica distorcida, com os dois ligantes dbso em posições *cis* e *trans*, respectivamente.

The reaction of the ambidentate ligand dibenzylsulfoxide (dbso) with Me$_2$SnCl$_2$ in 1:1 molar ratio leads to the formation of the five-coordinate adduct [Me$_2$SnCl$_2$(dbso)], whereas the same reaction conditions with Ph$_2$SnCl$_2$ provide the six-coordinate adduct *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$]. On the other hand, the reaction with ^{n}Bu$_2$SnCl$_2$ forms the dimeric adduct [{^{n}Bu$_2$SnCl$_2$(dbso)}$_2$], which probably possesses octahedral tin(IV) nuclei and bridging chlorides. The adducts [MeSnCl$_3$(dbso)$_2$] and [Ph$_3$SnCl(dbso)] were also prepared and included in the study. All complexes were studied by microanalysis and IR, NMR (^{1}H, ^{13}C and ^{119}Sn) and Mössbauer spectroscopies to investigate their structural properties. The six-coordinate species *fac*-[MeSnCl$_3$(dbso)$_2$] and *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$] were also studied by single crystal X-ray diffractometry. These compounds crystallize in the orthorhombic, *Pbcn*, and monoclinic space group *P2$_1$/c*, respectively, as discrete neutral molecules with the tin(IV) atom in a distorted octahedral geometry and the two dbso ligands in *cis* and *trans* positions, respectively.

**Keywords:** sulfoxide complexes, organotin(IV) complexes, crystal structure analyses

Introduction

Organotin(IV) compounds have demonstrated to exhibit wide biological activity.[1,2] Insofar as many sulfoxides are also noteworthy for the same reasons,[3] a combination of the two chemistries is an interesting line to pursue. Diorganotin(IV) dihalides, and more particularly Me$_2$SnCl$_2$,

form well-known 1:2 adducts with Lewis bases.[4] However, both Me$_2$SnCl$_2$ and Ph$_2$SnCl$_2$ form 1:1 adducts[5-7] with monodentate ligands, but reports on the isolation of both 1:1 and 1:2 adducts are scarce.[8] The formation of 1:1 systems is curious and, surprisingly, neither the stoichiometry of the reactants nor the reaction conditions appear to exert much influence.[4] The 1:1 adduct, [Me$_2$SnCl$_2$(dbso)], whose X-ray structure is already known,[5] has been described as an authentic and unique five-coordinate trigonal bipyramidal

compound without any intermolecular contact. The structure of dbso is shown below.
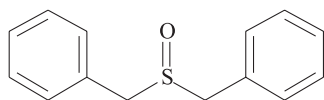
dbso

We report herein the preparation and spectroscopic investigation of five- and six-coordinate adducts involving $R_{4-m}SnCl_m$ (R = Me, ^nBu, Ph; and m = 1, 2, 3) and dibenzylsulfoxide (dbso). The X-ray diffraction study of the adducts *trans*-dichloro-*trans*-bis(dibenzylsulfoxide)-*trans*-diphenyltin(IV), *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$], and *fac*-trichloro-*cis*-bis(dibenzylsulfoxide)methyltin-(IV), *fac*-[MeSnCl$_3$(dbso)$_2$], is also presented.

Experimental

Material and procedures

All starting compounds and reagents were of highest grade and were used without purification. IR spectra were recorded from KBr pellets on a Bomem MB100 FT-IR spectrometer in the 4000-400 cm^{-1} region. (^{1}H, ^{13}C, ^{119}Sn) NMR spectra were run on a Varian Mercury Plus 300 MHz spectrophotometer, using CDCl$_3$ as solvent. Chemical shifts (ppm) are relative to TMS and Me$_4$Sn. ^{119}Sn Mössbauer spectra were collected at 77 K in the transmission geometry, on a conventional constant-acceleration spectrometer with a CaSnO$_3$ source kept at room temperature. All isomer shift values reported in this work are given with respect to this source. All Mössbauer spectra were computer-fitted assuming Lorentzian line shapes and the resulting isomer shifts and quadrupole splittings are accurate to *ca.* ± 0.05 mm s^{-1}. The velocity calibration of the instrument was done at room temperature with ^{57}Fe enriched foil. The microanalyses were performed using a FISSONS CHNS, model EA 108 microanalizer.

Single-crystals of *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$] and *fac*-[MeSnCl$_3$(dbso)$_2$], suitable for X-ray studies, were obtained at room temperature as colourless solids by slow evaporation from EtOH/CHCl$_3$ (3:1, v/v) and Me$_2$CO solutions, respectively. The data collection of *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$] was performed using an Enraf-Nonius Kappa CCD diffractometer[9] (Mo-K$_\alpha$ radiation) with cold N$_2$ gas cooling of the sample crystal. Diffraction data for *fac*-[MeSnCl$_3$(dbso)$_2$] were collected using an Enraf-Nonius CAD-4 diffractometer[10] (Cu-K$_\alpha$ radiation) at room

temperature, and data reduction was performed using the XCAD-4 program.[11]

Synthesis

Ph$_3$SnCl (0.5 g, 1.3 mmol) and dbso (0.3 g, 1.3 mmol) were dissolved in EtOH (30 mL). The solution was stirred at 70 °C for 2 h. The hot colorless solution was then left to stand at room temperature to evaporate the solvent and colorless crystals of [Ph$_3$SnCl(dbso)] were separated. All the other diorgorganotin(IV) adducts were obtained by slow evaporation of a CHCl$_3$ solution containing the appropriate diorganotin(IV) dihalide and dbso in 1:1 molar ratio; the products were then recrystallized from a suitable solvent. Attempts to prepare [Me$_2$SnCl$_2$(dbso)$_2$] (1:2) and [Ph$_2$SnCl$_2$(dbso)] (1:1) were unsuccessful.

dbso: ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.43–7.26 (m, 10H, –Ph); 3.92 (dd, J 12 and 15 Hz, 4H, –CH$_2$–Ph). ^{13}C-NMR (300 MHz, CDCl$_3$): δ 57.1 (C–Ph), 130.0 (*o*-C), 128.8 (*p*-C), 128.8 (*m*-C), 128.2 (*q*-C).

[Me$_2$SnCl$_2$(dbso)]: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.43–7.26 (m, 10H, –Ph); 3.97 (dd, J 13 and 14 Hz, 4H, –CH$_2$–Ph); 1.06 (s, 6H, Sn–CH$_3$, ^2J(^{119}Sn–^{1}H) = 75.3 Hz). ^{13}C NMR (300 MHz, CDCl$_3$): δ 130.3 (*o*-C), 129.0 (*p*-C), 128.8 (*m*-C), 128.7 (*q*-C); 55.8 (C–Ph), 9.9 (Sn–C, ^1J(^{119}Sn–^{13}C) = 568 Hz). Anal. calcd. for C$_{16}$H$_{20}$Cl$_2$OSSn: C, 42.71; H, 4.48; S, 7.12%. Found: C, 41.24; H, 4.64; S, 7.18%. Yield 90%; m.p. 117–118 °C.

[Ph$_2$SnCl$_2$(dbso)$_2$]: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.76–7.23 (m, 30H, –Ph); 3.89 (dd, J 15 and 18 Hz, 4H, –CH$_2$–Ph). ^{13}C NMR (300 MHz, CDCl$_3$): δ 130.3 (*o*-C), 129.2 (*p*-C), 129.0 (*m*-C), 128.6 (*q*-C); 55.9 (C–Ph). Anal. calcd. for C$_{40}$H$_{38}$Cl$_2$O$_2$S$_2$Sn: C, 59.72; H, 4.76; S, 7.97%. Found: C, 59.61; H, 4.81; S, 8.09%. Yield 60%; m.p. 127–128 °C.

[^{n}Bu$_2$SnCl$_2$(dbso)]: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.43–7.26 (m, 10H, –Ph); 3.93 (dd, J 12 and 15 Hz, 4H, –CH$_2$–Ph); 1.77 (m, 4H, –CH$_2$–Ph); 1.77 (m, 4H,–CH$_2$–Sn); 1.39 (m, 8H,); 0.94 (t, 6H, Sn–C–C–CH$_3$). ^{13}C NMR (300 MHz, CDCl$_3$): δ 130.2 (*o*-C), 129.1 (*p*-C), 129.0 (*m*-C), 128.7 (*q*-C); 55.1 (C–Ph), Sn–C(28.9)–C(27.0)–C(26.2)–C(13.5). Anal. calcd. for C$_{22}$H$_{32}$Cl$_2$OSSn: C, 49.47; H, 6.04; S, 6.00%. Found: C, 48.21; H, 6.09; S, 6.21%. Yield 80%; m.p. 110–112 °C.

[MeSnCl$_3$(dbso)$_2$]: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.40–7.25 (m, 10H, –Ph); 4.02 (s, 4H, –CH$_2$–Ph); 1.24 (s, 3H, Sn–CH$_3$, ^2J(^{119}Sn–^{1}H) = 123 Hz). ^{13}C NMR (300 MHz, CDCl$_3$): δ 130.6 (*o*-C), 129.1 (*p*-C), 129.0 (*m*-C), 128.0 (*q*-C). Anal. calcd. for C$_{29}$H$_{31}$Cl$_3$O$_2$S$_2$Sn: C, 49.71; H, 4.46; S, 9.15%. Found: C, 49.28; H, 4.72; S, 9.31%. Yield 70%; m.p. 147–149 °C.

[Ph₃SnCl(dbso)]: ¹H NMR (300 MHz, CDCl₃): δ 7.80 – 7.20 (m, 25H, –Ph); 3.80 (dd, *J* 15 and 21 Hz, 4H, –CH₂–Ph).¹³C NMR (300 MHz, CDCl₃): δ 130.1 (*o*-C), 129.7 (*p*-C), 128.9 (*m*-C), 128.4 (*q*-C); 56.6 (C–Ph). Anal. calcd. for C₃₂H₂₉ClOSSn: C, 62.42; H, 7.75; S, 5.21%. Found: C, 61.04; H, 7.81; S, 5.19%. Yield 50%; m.p. 101–103 °C.

Crystal structure determination

The initial structure solutions were obtained by the heavy-atom method using the SHELXS-97 program.¹² The other non-H atoms positions were obtained by difference Fourier maps. Hydrogen atoms were placed in geometric positions with C–H distances in the range of 0.93–0.99 Å and refined with a riding model with their U$_{iso}$ proportional to U$_{eq}$ of their parent atoms. Non-H atoms were refined with anisotropic displacement parameters. For the adduct *trans*-[Ph₂SnCl₂(dbso)₂], no correction for absorption was applied, and in *fac*-[MeSnCl₃(dbso)₂] the rings were refined as idealized rigid groups with C–C bond distances of 1.39 Å. All refinements were performed with full-matrix least-squares on F², using the SHELXL-97 program.¹³ The data of *fac*-[MeSnCl₃(dbso)₂] were corrected for absorption using the numerical method (Gaussian), with minimum and maximum transmission coefficients of 0.103 and 0.230, respectively. The crystal data and details of data processing are given in Table 1.

Results and discussion

The structure of trans-[Ph₂SnCl₂(dbso)₂]

The molecular structure with the labelling scheme is shown in Figure 2 and the selected bond distances and angles are listed in Table 2. The arrangement about tin(IV) in *trans*-[Ph₂SnCl₂(dbso)₂] is best described as a distorted octahedron geometry, in which the dbso molecules are well adapted for *trans* coordination. The coordination sphere is completed by two *trans*-phenyl and two *trans*-chloride groups and a slight distortion of the octahedron is observed. Thus, the angle C31^i–Sn1–C31 is 177.3(3)°, and the other two *trans* bond angles O1^i–Sn1–O1 and Cl1–Sn1–Cl2 are 174.0(2) and 180°, respectively. The last angle indicates that the adduct possesses crystallographic two-fold axial symmetry with tin(IV) and both Cl atoms lying on the crystallographic two-fold axis. It is interesting to compare our results with literature data for the five-coordinate adduct [Me₂SnCl₂(dbso)].⁵ In *trans*-[Ph₂SnCl₂(dbso)₂], the bond distance Sn1–O1 of 2.258(4) Å is significantly shorter than the equivalent bond distance value of 2.319(10) Å observed in [Me₂SnCl₂(dbso)], indicating a stronger interaction in

Ph₂Sn²⁺/dbso than in Me₂Sn²⁺/dbso. On the other hand, the Sn1–C31, 2.147(6); Sn1–Cl1, 2.578(2); and Sn1–Cl2, 2.509(2) Å bond lengths are considerably longer than the Sn1–C1, 2.128(15); Sn1–C2, 2.109(16); Sn1–Cl1, 2.392(6); and Sn1–Cl2, 2.464(6) Å bond lengths found in [Me₂SnCl₂(dbso)], as expected. The arrangement of the dbso ligands differs from that observed by Nardelli and collaborators¹⁴ in *cis*-dichloro-*cis-bis*(dimethylsulfoxide)-*trans*-diphenyltin(IV), *cis*-[Ph₂SnCl₂(dmso)₂], which has the chlorine atoms and the oxygen atoms *cis*, and the carbon atoms *trans*.

A sulfoxide coordinated to a metal *via* the oxygen atom can be represented formally by an R₂S$^{δ+}$–O$^{δ-}$ dipolar form, and coordination to an organotin(IV) species would be expected to lengthen the S–O bond. This lengthening is observed in most organotin(IV)–sulfoxide complexes.⁵,¹⁵ This is corroborated by IR spectroscopy, which shows a lowering of ν(S–O) from 1033 to 969-988 cm⁻¹ for all complexes under study here.

The structure of fac-[MeSnCl₃(dbso)₂]

The molecular structure with the labelling scheme is shown in Figure 1 and the selected bond distances and angles are listed in Table 2. The arrangement about tin(IV) in *fac*-[MeSnCl₃(dbso)₂], located in a general position of the space group *P2₁/c*, is a distorted octahedral geometry in which the three chlorides are arranged in a *facial* fashion and the dbso ligands are bonded by O atoms *cis* to one another. The *trans* position to the methyl group is occupied by a chlorine atom and not by the sulfoxide ligand, as observed in *mer*-[EtSnI₃(dpso)₂]¹⁶ (dpso = diphenylsulfoxide). However, the adducts *mer*-[MeSnCl₃(ImSOMe)], ImSOMe = 1-methyl-2-(methylsulfinylimidazole), and *mer*-[MeSnCl₃(PySO^{n}Pr)], PySO^{n}Pr = 2-(*n*-propylsulfinyl)pyridine, possess three chlorides arranged in a *meridional* position and the methyl group is *trans* to the N atom.¹⁷
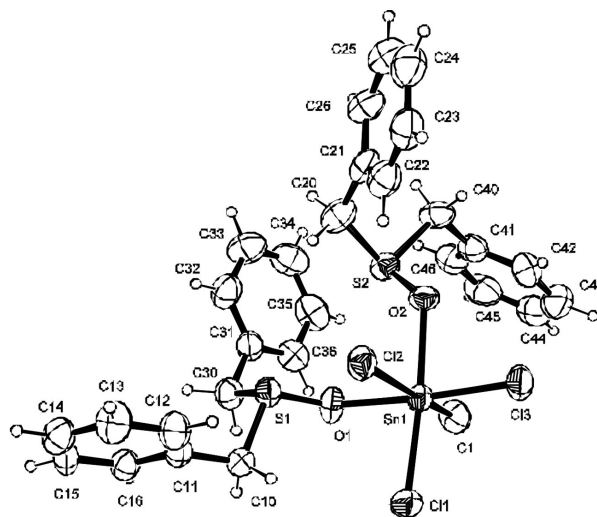
In Table 2, the Sn1–Cl1, Sn1–Cl2 and Sn1–Cl3 distances are given as 2.429(2), 2.399(2) and 2.422(2) Å, respectively. Therefore, the average of the Sn1–Cl1 and Sn1–Cl3 bond lengths (Cl *trans* to the dbso ligand) is 2.426(2) Å, and 2.426 – 2.399 = 0.027 Å. The O–Sn–O bonds [2.203(5) and 2.241(7) Å] form an angle of 92.6(3)° at the metal and the S–O bonds lengths [1.523(8) and 1.522(5) Å] are otherwise not much different from those bonds observed in other mono-organotin(IV) adducts containing sulfoxide as ligand.¹⁶,¹⁷ The [Sn–C 2.142(8) Å] bond distance is longer than those found in *mer*-[MeSnCl₃(ImSOMe)] [2.122(4) Å] and in *mer*-[MeSnCl₃(PySO^{n}Pr)] [2.110(7) Å], but it is shorter than the Sn–C [2.218(5) Å] found in *mer*-[EtSnI₃(dpso)₂].¹⁶

Table 1. Crystal data and structure refinement

Compound	*trans*-[Ph$_2$SnCl$_2$(dbso)$_2$]	*fac*-[MeSnCl$_3$(dbso)$_2$]
Empirical formula	C$_{40}$H$_{38}$Cl$_2$O$_2$S$_2$Sn	C$_{29}$H$_{31}$Cl$_3$O$_2$S$_2$Sn
Formula weight	804.45	700.98
Temperature (K)	100(2)	297(2)
Wavelength (Å)	0.71073	1.54180
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbcn*	*P*2$_1$/*c*
Crystal color/habit	Colourless/prism	Colourless/prism
a (Å)	14.347(1)	9.182(4)
b (Å)	10.259(1)	19.281(4)
c (Å)	23.661(1)	18.057(5)
β (deg.)		104.44(2)
Volume (Å^3)	3482.6(4)	3095.7(17)
Z	4	4
Calculated density (g cm^{-3})	1.534	1.503
Absorption coefficient (mm^{-1})	1.043	1.041
Crystal size (mm)	0.15 x 0.10 x 0.06	0.40 x 0.20 x 0.20
Theta range for data collection (°)	2.23 to 27.85	3.41 to 68.04
Index ranges	−18 ≤ *h* ≤ 18 −13 ≤ *k* ≤ 0 0 ≤ *l* ≤ 30	−11 ≤ *h* ≤ 9 −23 ≤ *k* ≤ 4 0 ≤ *l* ≤ 21
Reflections collected	7475	6420
Independent reflections	3953 [*R*(int) = 0.0462]	5551 [*R*(int) = 0.0826]
Data/restraints/parameters	3953/0/215	5551/0/294
Goodness-of-fit on *F*^{2}	1.132	1.045
Final *R* indices [*I* > 2σ(*I*)]	*R*$_1$ = 0.0530, *wR*$_2$ = 0.1659	*R*$_1$ = 0.0650, *wR*$_2$ = 0.1751
R indices (all data)	*R*$_1$ = 0.0901, *wR*$_2$ = 0.1906	*R*$_1$ = 0.1029, *wR*$_2$ = 0.1996
Extinction coefficient	0.0018(4)	0.0008(1)
Largest diff. peak and hole (e Å^{-3})	1.463 and −1.636	1.044 and −1.402

Figure 1. View of *fac*-[MeSnCl$_3$(dbso)$_2$] with the displacement parameters drawn at the 30% probability level.
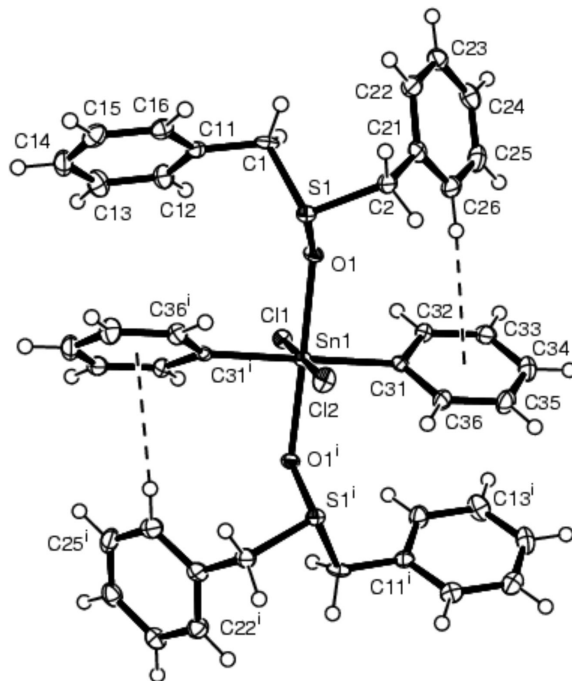
Figure 2. View of *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$], with ellipsoids drawn at the 50% probability level and hydrogen atoms as spheres of arbitrary radii. The dashed lines indicate intramolecular C–H⋯π contacts. [Symmetry code: (i) –x + 1, y, –z + ½].

Infrared spectroscopy

Table 3 lists the most important IR data, allowing several conclusions. The dbso ligand always binds to the tin(IV) moiety through the oxygen atom, as shown by the shift of ν(S–O) to lower values as compared to the free base. The ν(Sn–O) bands appear at 483 cm^{-1} for *fac*-[MeSnCl$_3$(dbso)$_2$], at 460 cm^{-1} for *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$] and at 455 cm^{-1} for [Ph$_3$SnCl(dbso)], in accordance with reported work related to ambidentate sulfoxides bonded to tin(IV).[18] However, the ν(Sn–O) absorptions in five-coordinate diorganotin(IV)–

sulfoxide adducts have been reported in the 415-440 cm^{-1} range.[19] The ν(C=C), δ(C–H) and δ(C=C) stretching vibrations do not show any appreciable alteration, indicating that the benzyl groups are far from the coordination center.

(*^{1}H, ^{13}C, ^{119}Sn) NMR spectroscopy*

The assignment of the ^{1}H and ^{13}C chemical shifts is presented in the experimental section, and coupling

constants, $^1J(^{119}Sn–^{13}C)$ and $^2J(^{119}Sn–^1H)$, and chemical shifts, $\delta(^{119}Sn)$, of our adducts, as well as of other compounds from the literature, are shown in Table 4. The NMR coupling constants $^1J(^{119}Sn–^{13}C)$ and $^2J(^{119}Sn–^1H)$ for compound **5**, which was crystallographically characterized[5] as being a five-coordinate tin(IV) adduct, were observed at 568 and 72 Hz, respectively. However, the adduct **6**, which has higher coupling constants values of 888 and 92 Hz, is formed by six-coordinate tin(IV) atoms. In view of this, the coupling constants values for adducts **1-3** indicate that, in $CDCl_3$ solution, they are no longer octahedral as in the solid state, but undergo a structural

change, showing five-coordinate behavior. In addition to that, the coupling constants for adduct **7** are considerably larger than those for adducts **1-5**, indicating that higher $^1J(^{119}Sn–^{13}C)$ and $^2J(^{119}Sn–^1H)$ values tend to correlate with higher coordination numbers (see Table 4). This can be attributed, at least partially, to a tendency to maximize the *s*-character in the C–Sn–C bonds in six-coordinate derivatives.[20] Applying the equation $^1J(^{119}Sn–^{13}C) = 11.4\,\theta – 875$, and our observed coupling constant of 568 Hz to adduct **5**, whose X-ray structure is known, we find the value of 127° for the (C–Sn–C) angle θ of adduct **5**, only 9° lower than the angle of 136.4(9)° reported by Ng and Rheingold[4] (Table 4). The NMR data for the 1:1 adduct [$Me_2SnCl_2(Hmimt)$] [Hmimt = 1-methyl-2(3H)-imidazolinethione], whose X-ray structure shows it to be a trigonal bipyramid,[21] present some similarity with the data for adduct **5**. The reported values of $^1J(^{119}Sn–^{13}C)$, $^2J(^{119}Sn–^1H)$, δ (^{119}Sn) and θ(C–Sn–C) for this compound are 491, 71 Hz, +19 ppm and 133°, respectively.

The coupling constant $^2J(^{119}Sn–^1H)$ value of 123 Hz found for *fac*-adduct **18** is only 8 Hz higher than that found for *fac*-adduct **16** and it is almost equal to that of 124 Hz found for *mer*-adduct **17**. This observation indicates that this behavior may be due more to an electronic rather than to a structural effect, wherein the oxygen atom in BtSOMe exhibits a higher electronic donor effect than the oxygen in dbso. Thus the tin(IV) atom would be more shielded in **18** than in **16**. This behaviour is also observed in ^{119}Sn-NMR spectroscopy.

^{119}Sn chemical shifts were found to lie between *ca.* –90 and –330 ppm in five-coordinate dimethyltin(IV) chelates.[22] However, the values for adducts **1-5** (Table 4) are completely out of this range, indicating that the presence of chlorine atoms in the coordination sphere of the tin(IV) nucleus shifts the signal towards much more deshielded values. In diphenyltin(IV) derivatives, (adducts **8-10** and **12**), the chemical shift values were found as usual, *i. e.*, at lower frequencies than in dimethyltin(IV) adducts, in spite

Table 2. Selected bond lengths [Å] and angles [°]

trans-[Ph₂SnCl₂(dbso)₂]		*fac*-[MeSnCl₃(dbso)₂]	
Sn1–C31	2.147(6)	Sn1–C1	2.142(8)
Sn1–O1	2.258(4)	Sn1–O1	2.203(5)
Sn1–Cl2	2.509(2)	Sn1–O2	2.241(7)
Sn1–Cl1	2.578(2)	Sn1–Cl1	2.429(2)
Sn1–O1	2.258(4)	Sn1–Cl2	2.399(2)
S1–O1	1.524(4)	Sn1–Cl3	2.422(2)
S1–C1	1.815(5)	S1–O1	1.529(5)
S1–C2	1.829(5)	S2–O2	1.523(8)
C31–Sn1–C31ⁱ	177.3(3)	C1–Sn1–Cl3	96.4(3)
C31–Sn1–O1ⁱ	91.5(2)	O1–Sn1–Cl3	175.8(2)
C31–Sn1–O1	88.3(2)	O2–Sn1–Cl3	83.7(2)
O1ⁱ–Sn1–O1	174.0(2)	Cl2–Sn1–Cl3	92.43(8)
C31–Sn1–Cl2	91.4(1)	C1–Sn1–Cl1	99.0(3)
O1–Sn1–Cl2	93.0(1)	O1–Sn1–Cl1	88.3(2)
C31–Sn1–Cl1	88.6(1)	O2–Sn1–Cl1	168.0(2)
O1–Sn1–Cl1	87.0(1)	C1–Sn1–O1	85.6(3)
O1–S1–C1	103.0(2)	Cl2–Sn1–Cl1	88.07(8)
O1–S1–C2	105.7(2)	C1–Sn1–O2	93.0(3)
C1–S1–C2	101.5(3)	Cl3–Sn1–Cl1	95.00(9)

Symmetry code: (i) –x + 1, y, –z + ½.

Table 3. Selected infrared absorptions (cm⁻¹)

Compound	C.N.	ν(C=C)	ν(S=O)	Δν(S=O)	ν(Sn–O)	δ(C–H)	δ(C=C)
dbso	-	1493vs, 1455vs	1033vs	-	-	776vs	700vs
[Me₂SnCl₂·dbso] ᵃ	5	1496vs, 1458vs	988vs	45	-	775sh	697vs
[Ph₂SnCl₂·(dbso)₂] ᵇ	6	1494s, 1455s	984vs	49	460s	776vs	700vs
[ⁿBu₂SnCl₂·dbso]₂	6	1494vs, 1455vs	973vs	60	-	776vs	701vs
[MeSnCl₃·(dbso)₂] ᵃ	6	1496vs, 1455vs	950vs	83	483s	767vs	697vs
[Ph₃SnCl₂·dbso] ᶜ	5	1492s, 1452s	969vs	64	455s	775vs	698vs

Abbreviations and attributions: C.N. = coordination number; ᵃ νₐ(Sn–CH₃) = 572m cm⁻¹; νₛ(Sn–CH₃) = 516m cm⁻¹; ᵇ ν(C=C) = 1480s; 1430s cm⁻¹ (Sn–Ph); ᶜ ν(C=C) = 1478s, 1429s cm⁻¹ (Sn–Ph); ν = stretching; s = strong; vs = very strong; sh = shoulder; m = medium; δ = out of plane deformation.

of the greater electron donation properties of the methyl groups compared to phenyl.[23] This observed dependence of the chemical shift of the tin(IV) atom on the nature of the diorganotin(IV) derivative can be related to the relative polarity of the Sn–C bonds. The polarity of these bonds depends on the amount of residual positive charge located on tin, as well as on the *s*-character of tin(IV) in these bonds.[24] Accordingly, more residual positive charge is localized on the central tin(IV) atom in Ph_2Sn^{2+} compared to Me_2Sn^{2+}. Therefore, more shielding is expected on the tin(IV) atom in the five-coordinate diphenyltin(IV) derivative. The ^{119}Sn chemical shift value of −167 ppm, observed for adduct **14**, is inside the range of −125 to −515 ppm observed for six-coordinate diorganotin(IV) chelates.[22]

Mössbauer spectroscopy

^{119}Sn Mössbauer spectral parameters of the dbso derivatives are reported in Table 5, which includes parameters from the literature for comparison. The spectra of the adducts **2**, **7**, **13** and **19** are shown in Figure 3.

The isomer shift (δ) is very sensitive to the first coordination sphere and depends on the nature and number of organic groups bonded to the tin(IV) atom.[28,29] This parameter is correlated to the change of *s*-electron density on the metal by means of the +I inductive effect imposed by the ligands. A result of this is the inverse dependence of δ with electronegativity.[30] Thus δ increases on replacing the phenyl by the alkyl groups in the coordination sphere of tin(IV). This increase in δ can be seen (Table 5) starting with the adducts **17-20** derived from $MeSnCl_3$ (0.89–0.97 mm s^{-1}), including the adducts **12-16** derived from Ph_2SnCl_2 (1.26-1.39 mm s^{-1}), and finishing with the adducts **1-6** derived from Me_2SnCl_2 (1.35-1.47 mm s^{-1}). The adduct **7** derived from $^nBu_2SnCl_2$ (1.63 mm s^{-1}) confirms that isomer shifts increase in the sequence $Ph_2Sn^{2+} < Me_2Sn^{2+} < ^nBu_2Sn^{2+}$ (see Table 5).

The quadrupole splitting (Δ) values summarized in Table 5 show that this parameter can potentially throw light upon the question of which is the correct coordination number of the tin(IV) atom in adducts formed from diorganotin(IV) dichloride and monodentate ligands. The Δ value of adduct **1** (3.52 mm s^{-1}) is typical of dimethyltin(IV) adducts with a distorted trigonal bypyramidal geometry around the tin(IV) atom, as supported by the crystal structure determination: an authentic five-coordinate trigonal bipyramidal compound[5]

Table 4. (^1H, ^{13}C)-NMR coupling constants (*J*, Hz) and ^{119}Sn-NMR chemical shifts (δ, ppm)

Adduct	C.N.	$^2J(^{119}Sn–^1H)$	$^1J(^{119}Sn–^{13}C)$	$\delta(^{119}Sn)$
1. $[Me_2SnCl_2(^nPrSOCH_2)_2]$ [a]	5, 6 [h]	78	595	+9
2. $[\{^nBu_2SnCl_2(dbso)\}_2]$ [b]	5, 6 [h]	-	-	+42
3. $[\{Me_2SnCl_2(PhSOCH_2)_2\}_n]$ [a]	5, 6 [h]	71	-	+59
4. $[Me_2SnCl_2(BtSOMe)]$ [c]	5	72	538	+99
5. $[Me_2SnCl_2(dbso)]$ [b]	5	72	568	+100
6. *trans*-$[Me_2SnCl_2(ImSOMe)]$ [d]	6	92	888	-8
7. *trans*-$[Me_2SnCl_2(dmso)_2]$ [e]	6	86	1060	-
8. $[Ph_2SnCl_2(ImSOMe)]$ [d]	5	-	-	-36
9. $[Ph_2SnCl_2\{(CH_2)_3SOCH(Ph)SO\}]$ [f]	5	-	-	-62
10. $[Ph_2SnCl_2(BtSOMe)]$ [c]	5	-	-	-63
11. $[Ph_3SnCl(dbso)]$ [b]	5	-	-	-67
12. $[Ph_2SnCl_2(PySO^nPr)]$ [g]	5	-	-	-108
13. *trans*-$[\{Ph_2SnCl_2(PhSOCH_2)_2\}_n]$ [a]	6	-	-	-129
14. *trans*-$[Ph_2SnCl_2(dbso)_2]$ [b]	6	-	-	-167
15. $[\{Ph_2SnCl_2(^nPrSOCH_2)_2\}_n]$ [a]	6	-	-	-168
16. *fac*-$[MeSnCl_3(BtSOMe)_2]$ [c]	6	115	538	-214
17. *mer*-$[MeSnCl_3(PySO^nPr)]$ [g]	6	124	-	-350
18. *fac*-$[MeSnCl_3(dbso)_2]$ [b]	6	123	-	-368

Abbreviations and attributions: C.N. = coordination number; BtSOMe = 2-(methylsulfinyl)benzothiazole; ImSOMe = 1-methyl-2-(methylsulfinyl)imidazole; (CH$_2$)$_3$SOCH(Ph)SO = 2-phenyl-1,3-dithiane-*trans*-1-*trans*-3-dioxide; PySO^{n}Pr = 2-(*n*-propylsulfinyl)pyridine; dmso = dimethylsulfoxide; [a] reference 25; [b] this work; [c] reference 19; [d] reference 26; [e] reference 27; [f] reference 6; [g] reference 26; [h] Coordination number in solid state.

without any short intermolecular contact. The parameters $\delta = 1.45$; $\Delta = 3.13$ mm s^{-1} and the angle θ (C–Sn–C) = 133° have been reported for the related adduct with analogous coordination geometry, namely [Me$_2$SnBr$_2$(Hmimt)].[21] The larger Δ value of adduct **2** (3.84 mm s^{-1}), compared to **1** (3.52 mm s^{-1}), is due to the considerable intermolecular contact [S=O···Sn 2.75(1) Å], which makes this distance much shorter than the sum of the van der Waals[31] radii of the two atoms, r_{Sn} = 2.2, r_o = 1.5 Å. Thus, the C–Sn–C angle is opened up to 154.7(3)°, to complete the distorted *trans*-C–Sn–C skeleton.[16] The differences observed in Δ values ranging from 3.54-4.16 mm s^{-1} for adducts **4-7**, compared to adducts **1** and **3**, are considerable (Table 5). Therefore, this means that these compounds (**4-7**) possess the same geometry around the tin(IV) atom, which corresponds to six-coordinated structures, as supported by X-ray diffraction for **4**,[19] **5**,[32] and **6**.[33] In view of this, the Mössbauer spectra of the adducts **8-11** show a doublet with values of Δ ranging from 2.92-3.22 mm s^{-1}, indicating five-coordinated tin(IV) compounds, whereas the spectra of **12-16** show values ranging from

3.51–3.98 mm s^{-1}, which are typical of six-coordinated tin(IV) derivatives.

The geometry about tin(IV) in adducts **17** ($\Delta = 2.13$ mm s^{-1}) and **18** ($\Delta = 2.07$ mm s^{-1}) is that of a distorted octahedron environment, with the SnCl$_3$$^+$ skeleton arranged in *facial* mode (Figure 1). On the other hand, in the octahedral adducts **19** ($\Delta = 1.95$ mm s^{-1}) and **20** ($\Delta = 1.69$ mm s^{-1}), the SnCl$_3$$^+$ skeleton is organized in a *meridional* position with the methyl group *trans* to the nitrogen atom in both compounds.[17] In view of this, we believe that the magnitude of Δ can be used to distinguish between *fac-* and *mer-*arrangements as more crystallographic data become available.

From the Δ value and the point-charge approach, the equation $\Delta = -4 [R] (1 - 0.75 \sin^2 \theta)^{1/2}$ gives an estimate of θ, where (θ, deg) is the C–Sn–C bond angle[34] and [R] is the partial quadrupole splitting (pqs) of the group, arising either from the alkyl or the aryl groups. For five- and six-coordinated tin(IV), the working values used for [Me] and [Ph] were –1.13 and –0.95 mm s^{-1}, respectively.[34,35] The calculated bond angle values of 134° for **1** and 180° for **12** reveal trigonal bipyramidal (TBP) and

Table 5. Mössbauer data and C–Sn–C angles (°)

Adduct	C.N.	δ (mm s^{-1})	Δ (mm s^{-1})	C–Sn–C (exp.)
1. [Me$_2$SnCl$_2$(dbso)] [a]	5	1.38	3.52	136.4(9) [h]
2. [Me$_2$SnCl$_2$(ImSOMe)] [b]	5	1.47	3.84	154.7(3) [i]
3. [Me$_2$SnCl$_2$(BtSOMe)] [c]	5	1.39	3.52	-
4. *trans*-[Me$_2$SnCl$_2$(dmso)$_2$] [d]	6	1.40	4.16	170(2) [j]
5. *trans*-[{Me$_2$SnCl$_2$(*n*PrSOCH$_2$)$_2$}$_n$] [e]	6	1.38	3.73	172.3(2) [k]
6. *trans*-[{Me$_2$SnCl$_2$(PhSOCH$_2$)$_2$}$_n$] [e]	6	1.35	3.54	165.2(2) [l]
7. *trans*-[{*n*Bu$_2$SnCl$_2$(dbso)}$_2$] [a]	6	1.63	4.06	-
8. [Ph$_2$SnCl$_2${(CH$_2$)$_3$SOCH(Ph)SO}] [f]	5	1.32	3.22	138.6(2)
9. [Ph$_2$SnCl$_2$(Bt)] [g]	5	1.36	2.92	132.5(7)
10. [Ph$_2$SnCl$_2$(BtSOMe)] [c]	5	1.27	2.97	-
11. [Ph$_3$SnCl(dbso)] [a]	5	1.32	3.19	-
12. *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$] [a]	6	1.32	3.98	177.3(3)
13. *trans*-[Ph$_2$SnCl$_2$(dmso)$_2$] [d]	6	1.27	3.95	167.2(2); 171.8(2) [m]
14. *trans*-[Ph$_2$SnCl$_2$(ImSOMe)] [b]	6	1.26	3.51	-
15. *trans*-[{Ph$_2$SnCl$_2$(*n*PrSOCH$_2$)$_2$}$_n$] [e]	6	1.39	3.63	-
16. *trans*-[{Ph$_2$SnCl$_2$(PhSOCH$_2$)$_2$}$_n$] [e]	6	1.28	3.73	-
17. *fac*-[MeSnCl$_3$(dbso)$_2$] [a]	6	0.92	2.13	-
18. *fac*-[MeSnCl$_3$(BtSOMe)$_2$] [g]	6	0.97	2.07	-
19. *mer*-[MeSnCl$_3$(ImSOMe)] [b]	6	0.91	1.95	-
20. *mer*-[MeSnCl$_3$(PySOPr^n)] [b]	6	0.89	1.69	-

Abbreviations and attributions: C.N. = coordination number; BtSOMe = 2-(methylsulfinyl)-benzothiazole; ImSOMe = 1-methyl-2-(methylsulfinyl) imidazole; (CH$_2$)$_3$SOCH(Ph)SO = 2-phenyl-1,3-dithiane-*trans*-1-*trans*-3-dioxide; PySO^{n}Pr = 2-(*n*-propylsulfinyl)pyridine; dmso = dimethylsulfoxide; [a] this work; [b] reference 26; [c] reference 19; [d] reference 36; [f] reference 6; [g] reference 37; [h] reference 5; [i] reference 16; [j] reference 38; [k] reference 32; [l] reference 33; [m] reference 14.
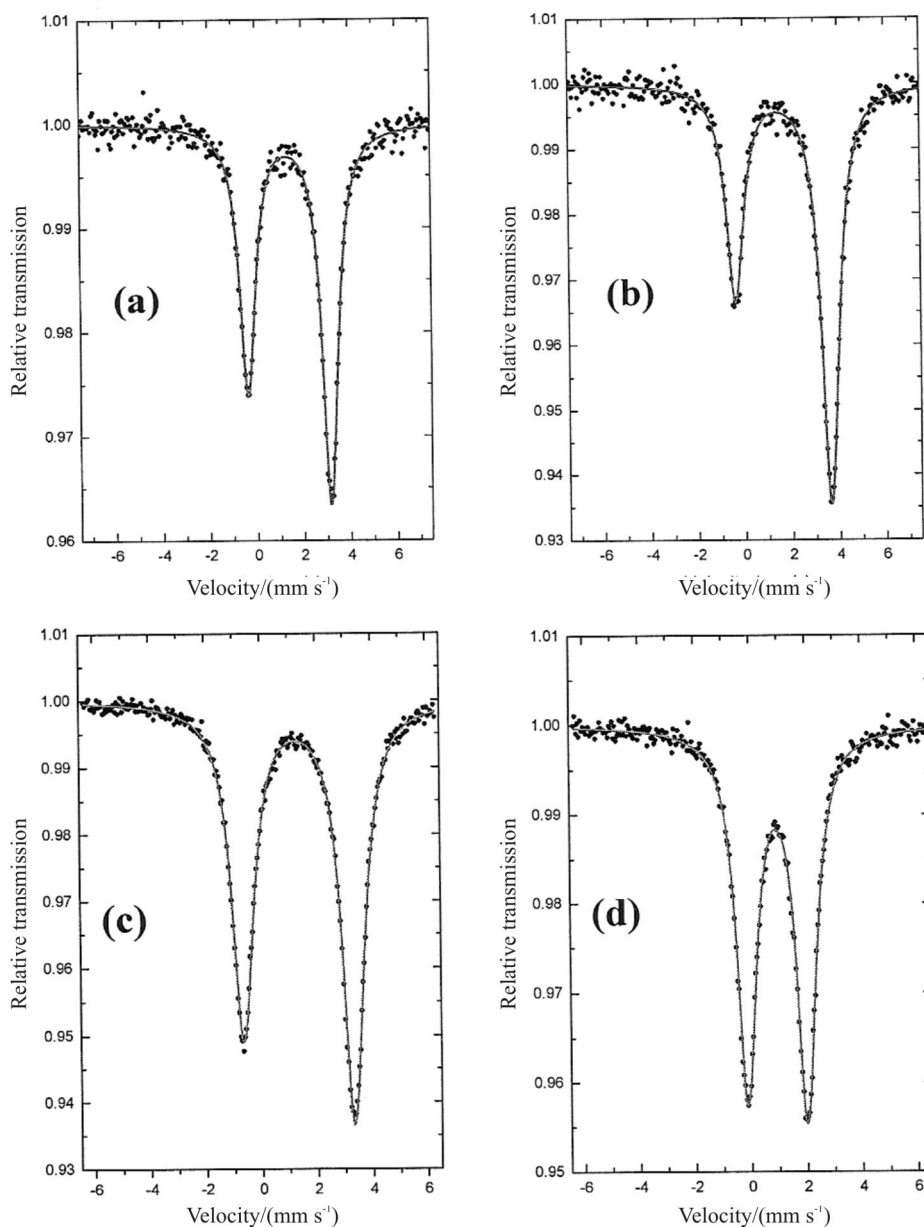
Figure 3. ^{119}Sn Mössbauer effect spectra obtained at 77 K for complexes [Me$_2$SnCl$_2$(dbso)] (**2**)-(a); [{^{n}Bu$_2$SnCl$_2$(dbso)}$_2$] (**7**)-(b); *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$] (**13**)-(c); and *fac*-[MeSnCl$_3$(dbso)$_2$] (**19**)-(d).

octahedral (O$_h$) arrangements around the tin(IV) atoms, respectively.

Supplementary Information

Crystallographic data for the structural analysis of the complexes have been deposited at the Cambridge Crystallographic Data Center, with the deposition numbers CCDC 619271 for *trans*-[Ph$_2$SnCl$_2$(dbso)$_2$] and CCDC 619272 for *fac*-[MeSnCl$_3$(dbso)$_2$]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, United Kingdom; Fax: +44 1223 336033, or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

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