Article

Different Coordination Modes for Disulfoxides towards Diorganotin(IV) Dichlorides. X-ray Crystal Structures of 1,2-*cis-bis*-(phenylsulfinyl)ethene (*rac-,cis*-cbpse) and Adducts [{Ph$_2$SnCl$_2$(*meso*-bpse)}$_n$] and [{*n*-Bu$_2$SnCl$_2$(pdtd)}$_2$]

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As reações de *meso*-1,2-*bis*(fenilsulfinil)etano (*meso*-bpse) com Ph$_2$SnCl$_2$, de 2-fenil-1,3-ditiona *trans*-1-*trans*-dióxido (pdtd) com *n*-Bu$_2$SnCl$_2$ e de 1,2-*cis-bis*-(phenylsulfinyl)etene (*rac-,cis*-cbpse) com Ph$_2$SnCl$_2$, na proporção molar 1:1, levaram à formação de [{Ph$_2$SnCl$_2$(*meso*-bpse)}$_n$], [{*n*-Bu$_2$SnCl$_2$(pdtd)}$_2$] e [{Ph$_2$SnCl$_2$(*rac,cis*-cbpse)}$_x$] (*x* = 2 ou *n*) respectivamente. Na investigação das propriedades estruturais dos produtos foram empregadas as espectroscopias de absorção no infravermelho, Mössbauer e RMN de ¹¹⁹Sn, além de análise elementar e difratometria de raios X em monocristal. O estudo de [{Ph$_2$SnCl$_2$(*meso*-bpse)}$_n$] por difratometria de raios X revelou a ocorrência de um encadeamento infinito no qual os átomos de tin(IV) apresentam uma geometria octaédrica distorcida com os átomos de Cl em posições *cis* e os grupos Ph em *trans*. A estrutura cristalina de [{*n*-Bu$_2$SnCl$_2$(pdtd)}$_2$] revelou a presença de espécies diméricas centrossimétricas nas quais os átomos de tin(IV) possuem geometria octaédrica distorcida com dissulfóxidos em ponte ocupando posições *cis* e grupos *n*-butila ocupando posições *trans*. Os dados espectroscópicos indicaram que o produto contendo o ligante *rac,cis*-cbpse pode ser dimérico ou polimérico. O estudo por difratometria de raios X do sulfóxido *rac-,cis*-cbpse livre revelou que os cristais pertencem ao grupo espacial *C2/c*.

The reactions of *meso*-1,2-*bis*(phenylsulfinyl)ethane (*meso*-bpse) with Ph$_2$SnCl$_2$, 2-phenyl-1,3-dithiane *trans*-1-*trans*-3-dioxide (pdtd) with *n*-Bu$_2$SnCl$_2$ and 1,2-*cis-bis*-(phenylsulfinyl) ethene (*rac-,cis*-cbpse) with Ph$_2$SnCl$_2$, in 1:1 molar ratio, yielded [{Ph$_2$SnCl$_2$(*meso*-bpse)}$_n$], [{*n*-Bu$_2$SnCl$_2$(pdtd)}$_2$] and [{Ph$_2$SnCl$_2$(*rac,cis*-cbpse)}$_x$] (*x* = 2 or *n*) respectively. All adducts were studied by IR, Mössbauer and ¹¹⁹Sn NMR spectroscopic methods, elemental analysis and single crystal X-ray diffractometry. The X-ray crystal structure of [{Ph$_2$SnCl$_2$(*meso*-bpse)}$_n$] revealed the occurrence of infinite chains in which the tin(IV) atoms appear in a distorted octahedral geometry with Cl atoms in *cis* and Ph groups in *trans* positions. The X-ray crystal structure of [{*n*-Bu$_2$SnCl$_2$(pdtd)}$_2$] revealed discrete centrosymmetric dimeric species in which the tin(IV) atoms possess a distorted octahedral geometry with bridging disulfoxides in *cis* and *n*-butyl moieties in *trans* positions. The spectroscopic data indicated that the adduct containing the *rac,cis*-cbpse ligand can be dimeric or polymeric. The X-ray structural analysis of the free *rac-,cis*-cbpse sulfoxide revealed that the crystals belong to the *C2/c* space group.

Keywords: Tin(IV) complexes, disulfoxide ligand, crystal structure

Introduction

Organotin(IV) compounds have been 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. The Lewis base *rac-,cis*-1,2-*bis*(phenylsulfinyl) ethene (*rac-,cis*-cbpse) is known to bond to different metal centres *via* either the O atoms, the S atoms or the olefinic (–HC=CH–) centre. An *O,O*-bonded chelate with

this ligand has been described for a typically 'hard' Lewis acid, namely Ph_3SnCl,[4] whereas the 'softer' platinum(II) species interacts exclusively with the S atoms to afford an *S,S*-bonded 5-membered ring.[5] On the other hand, the very soft platinum(0) site, interestingly, yielded yet another ligating mode, namely an η^2-alkene platinum(0) linkage.[6] It is thus apparent that the two factors, inherent basicity and hardness/softness, play a part in complex formation.[6]

Filgueiras and collaborators[4] have shown that the reactions of Ph_3SnCl with disulfoxides of the type *meso-*, *rac*-$PhSO(CH_2CH_2)SOPh$ [1,2-*bis*-(phenylsulfinyl) ethane: *meso-,rac*-bpse] and *rac-,cis*-$PhSO(HC=CH)$ $SOPh$ [1,2-*cis*-bis(phenylsulfinyl)ethene: *rac-,cis*-cbpse], in 1:1 ratio (acid:base), afford adducts of stoichiometry [Ph_3SnCl(*meso-,rac*-bpse)] and [Ph_3SnCl(*rac-,cis*-cbpse)], respectively. On the other hand, Zhu *et al.*[7] have reported the preparation and crystal structure of a bridged 2:1 (acid:base) bimetallic adduct of formula [$(Ph_3SnCl)_2$(*meso*-bpse)]. In contrast with these results, the X-ray structure of the adduct [{Me_2SnCl_2(*meso*-bpse)}$_n$] has been determined and revealed the occurrence of polymeric chains along the crystallographic *a* axis in which the ligand and organotin(IV) moiety alternate.[8]

(pdtd)   (*meso*-bpse)   (*rac-,cis*-cbpse)
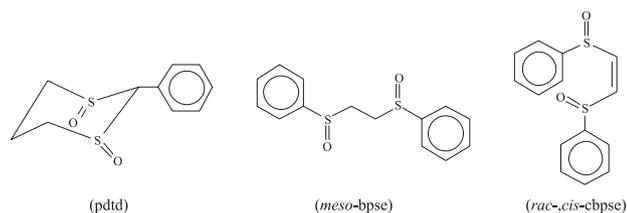
Herein, we describe the preparation and X-ray crystal structure of *rac-,cis*-cbpse and of the adducts [{Ph_2SnCl_2(*meso*-bpse)}$_n$] and [{n-Bu_2SnCl_2(pdtd)}$_2$], where the second compound shows an uncommon coordination mode of a disulfoxide (pdtd) towards a diorganotin(IV) dihalide, namely n-Bu_2SnCl_2. The spectroscopic data has shown that the adduct [{Ph_2SnCl_2(*rac-,cis*-cbpse)}$_x$] ($x = 2$ or n) possesses either dimeric or polymeric molecules. In spite of being bifunctional, pdtd, *meso*-bpse and *rac-,cis*-cbpse act as *bis*-monodentate ligands, as a result of their peculiar stereochemistry.

Experimental

Materials and methods

Solvents and diorganotin(IV) dichorides were commercially available (Aldrich) and were used as supplied. The disulfoxides pdtd, *meso*-bpse and *rac-,cis*-

cbpse were kindly provided by Prof. C. Celso, who had prepared them previously.[4] The adducts [Ph_2SnCl_2(*meso*-cbpse)] (m.p. 138-141 °C), [{n-Bu_2SnCl_2(pdtd)}$_2$] (m.p. 265–267 °C) and [{Ph_2SnCl_2(*rac-,cis*-cbpse)}$_x$] (m.p. 85-87 °C) were synthesized by the following procedure: equal amounts (0.50 mmol) of both the diorganotin(IV) dichloride and the appropriate sulfoxide were dissolved in EtOH. After refluxing for 1 h, the solution was filtered and a clear filtrate was obtained. Slow cooling and evaporation of the first two solutions afforded an abundant crop of colorless crystals (*ca.* 60% yield) appropriated for X-ray diffraction analysis. [{Ph_2SnCl_2(*meso*-bpse)}$_n$]: Found: C, 44.8; H, 3.4; S, 5.9. Calcd. for $C_{36}H_{34}Cl_4O_2S_2Sn_2$: C, 45.9, H, 3.6, S, 6.1%. [{n-Bu_2SnCl_2(pdtd)}$_2$]: Found: C, 40.3; H, 5.4; S, 12.2. Calcd. for $C_{36}H_{60}Cl_4O_4S_4Sn_2$: C, 40.6, H, 5.7, S, 12.0%. [{Ph_2SnCl_2(*rac-,cis*-cbpse)}$_x$] ($x = 2$ or n): Found: C, 49.5; H, 3.51; S, 9.8. Calcd. For $C_{52}H_{44}Cl_4O_4S_4Sn_2$: C, 50.3, H, 3.58, S, 10.3%.

Physical measurements

IR spectra were recorded on a Bomem MB100 FT-IR spectrophotometer in the 4000-400 cm^{-1} range using KBr pellets. ^{119}Sn, ^{1}H and ^{13}C NMR spectra were run on a Bruker Advance DRX 400 MHz spectrophotometer using $CDCl_3$. Chemical shifts are related to tetramethylsilane (tms) and $SnMe_4$. ^{119}Sn Mössbauer spectra were collected at 100 K in the transmission geometry on a constant-acceleration conventional spectrometer by using 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 microanalyses for C, H, N and S were performed in a Fissons EA 1108 elemental analyzer.

X-ray crystallography studies

Crystallographic data for *rac-,cis*-cbpse and adducts [{Ph_2SnCl_2(*meso*-bpse)}$_n$] and [{n-Bu_2SnCl_2(pdtd)}$_2$] are listed in Table 2. Selected bond distances and angles are presented in Table 3. Crystal data for all compounds were collected at 293(2) K on a Enraf-Nonius Kappa-CCD area detector diffractometer with graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). Data collections employed the COLLECT program,[9] integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system[10] and absorption corrections were carried out using the multi-scan method.[11]

Results and Discussion

IR spectroscopy

Table 1 shows the selected infrared data. The IR spectra of the disulfoxides (*meso*-bpse, pdtd and *rac*-,*cis*-cbpse) show very strong ν(S=O) absorptions at 1037, 1044 and 1040 cm^{-1}, respectively, which appear at 998, 981 and 965 cm^{-1} in the spectra of the corresponding adducts. This behavior is consistent with the fact that both S=O groups are bonded to the metal, causing the shift to lower frequency. The IR spectra of the adducts also show bands at 456 cm^{-1} for [{Ph$_2$SnCl$_2$(*meso*-bpse)}$_n$], at 413 cm^{-1} for [{^{n}Bu$_2$SnCl$_2$(pdtd)}$_2$] and at 459 cm^{-1} for [{Ph$_2$SnCl$_2$(*rac*-, *cis*-cbpse)}$_x$], which were assigned to the ν(Sn–O) vibration.[4] The $\Delta\nu$(S=O) value of 75 cm^{-1} calculated for *rac*-,*cis*-cbpse and its comparison with the 63 cm^{-1} shift for *meso*-bpse indicates that the unsaturated ligand is much more basic than the saturated one.[4]

NMR spectroscopy

The ^{1}H and ^{13}C NMR spectra for *rac*-,*cis*-cbpse in CDCl$_3$ show a singlet resonance at δ = 6.78 and δ = 144.0 ppm attributed, respectively, to the chemically and magnetically equivalent protons and carbons present in the ethylene (–HC=CH–) moiety. Regarding the ^{119}Sn NMR, the chemical shifts, δ(^{119}Sn), relative to SnMe$_4$ in six-coordinate organotin(IV) derivatives were found to lie between *ca.* –125 and –515 ppm,[12] whereas those from five-coordinate species from +25 to –319 ppm.[13] A series of five-coordinate diphenyltin(IV) complexes were found to have shifts from –62 to –276 ppm.[14] Therefore, the chemical shift values of +69 and –115 ppm found for [{n-Bu$_2$SnCl$_2$(pdtd)}$_2$] and [{Ph$_2$SnCl$_2$(*rac*-,*cis*-cbpse)}$_x$], respectively, are indicative of considerable shielding and five-coordination of the tin(IV) atoms. In view of this, in CDCl$_3$ solution both adducts are considerably dissociated, suggesting that the six-coordination pattern in the solid state has not remained in solution.

Mössbauer spectroscopy

^{119}Sn Mössbauer spectral parameters of the disulfoxide derivatives are reported in Table 1, which includes parameters from literature for comparison. The similarity among the quadrupole splittings (Δ) observed for [{Ph$_2$SnCl$_2$(*meso*-bpse)}$_n$] (3.73 mm s^{-1}), [{Me$_2$SnCl$_2$(*meso*-bpse)}$_2$] (3.54 mm s^{-1}), [{n-Bu$_2$SnCl$_2$(pdtd)}$_2$] (3.59 mm s^{-1}) and [{Ph$_2$SnCl$_2$(*rac*-,*cis*-cbpse)}$_x$] (3.71 mm s^{-1}) compared to [Ph$_2$SnCl$_2$(pdtd)] (Δ = 2.85 mm s^{-1}) may be accounted for by a greater asymmetry in the electronic density distribution around the tin(IV) in the first three adducts. These results indicate that [Ph$_2$SnCl$_2$(pdtd)] is five-coordinate, while the others are six-coordinate in the solid state.

The isomer shift (δ) is very sensitive to the first coordination sphere and is dependent on the nature and number of organic groups bonded to the tin(IV) nucleus. 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, and a result of this is the inverse dependence of δ with electronegativity.[15] Thus, δ increases on replacing the Ph by the Me groups in the coordination sphere of tin(IV), as given by the adducts [{Ph$_2$SnCl$_2$(*meso*-bpse)}$_n$] (1.28 mm s^{-1}) and [{Me$_2$SnCl$_2$(*meso*-bpse)}$_2$] (1.35 mm s^{-1}) (Table 1). The similarity in isomer shifts observed in [{n-Bu$_2$SnCl$_2$(pdtd)}$_2$] (1.49 mm s^{-1}) and in [{Ph$_2$SnCl$_2$(*rac*-,*cis*-cbpse)}$_x$] (1.50 mm s^{-1}) is noteworthy. The δ value of 1.50 mm s^{-1} may be a consequence of the much more basic behavior of the unsaturated *rac*-,*cis*-cbpse ligand compared to the saturated *meso*-cbpse ligand. These results are corroborated by IR and ^{119}Sn NMR spectroscopies. The lower value of δ found in the five-coordinate adduct [Ph$_2$SnCl$_2$(pdtd)] (δ = 1.32 mm s^{-1})[16] is a consequence of rehybridization (sp^3d) of tin(IV), which may be thought of as a linear combination of sp^2 and $p_z d_z^2$ orbitals. Thus, the equatorial Sn–C bonds will have greater *s*-character and smaller *p*-character, thereby decreasing the δ value.[17]

Table 1. Infrared absorptions, ^{119}Sn NMR chemical shifts and Mössbauer parameters for disulfoxides and tin(IV) adducts

Compound	ν(S=O), cm^{-1}	$\Delta\nu$(S=O), cm^{-1}	ν(Sn–O), cm^{-1}	δ (ppm)	δ (mm s^{-1})	Δ (mm s^{-1})
meso-bpse	1037					
[{Ph$_2$SnCl$_2$(*meso*-bpse)}$_n$][a]	998	39	456	–129	1.28	3.73
[{Me$_2$SnCl$_2$(*meso*-bpse)}$_n$][a]	978	59	465	+59	1.35	3.54
pdtd	1044					
[{n-Bu$_2$SnCl$_2$(pdtd)}$_2$][b]	1007, 981	63	413	+69	1.49	3.59
[Ph$_2$SnCl$_2$(pdtd)][c]	1040, 950	94	420	–62	1.32	2.85
rac-,*cis*-cbpse	1040					
[{Ph$_2$SnCl$_2$(*rac*-,*cis*-cbpse)}$_x$][b]	965	75	459	–115	1.50	3.71

[a] Ref. 18; [b] this work; [c] ref. 13

**Table 2.** Crystallographic data for *rac-,cis*-cbpse and tin(IV) adducts

	rac-,cis-cbpse	[{Ph$_2$SnCl$_2$(*meso*-bpse)}$_n$]	[{*n*-Bu$_2$SnCl$_2$(pdtd)}$_2$]
Formula	C$_{14}$H$_{10}$O$_2$S$_2$	C$_{26}$H$_{24}$Cl$_2$O$_2$S$_2$Sn	C$_{36}$H$_{60}$Cl$_4$O$_4$S$_4$Sn$_2$
M (g mol^{-1})	274.34	622.16	1064.30
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*P2$_1$/c*	*P2$_1$/n*
Crystal color	Colorless	Colorless	Colorless
Crystal size (mm)	0.08 x 0.08 x 0.24	0.16 x 0.19 x 0.29	0.10 x 0.18 x 0.25
a (Å)	14.1309(3)	20.7426(3)	9.1040(3)
b (Å)	8.8040(3)	12.66760(10)	16.9912(6)
c (Å)	10.8091(3)	20.2931(3)	15.2949(5)
β (°)	100.440(2)	97.6680(10)	95.270(2)
V (Å^3)	1322.48(6)	5284.51(12)	2355.93(14)
F (000)	568	2496	1062
Z	4	8	2
Calculated density (g cm^{-3})	1.378	1.564	1.479
Absorption coefficient (mm^{-1})	0.392	1.349	1.496
Limiting indices	$-18 \leq h \leq 18$	$-27 \leq h \leq 27$	$-12 \leq h \leq 11$
	$-11 \leq k \leq 11$	$-16 \leq k \leq 16$	$-21 \leq k \leq 21$
	$-14 \leq l \leq 14$	$-23 \leq l \leq 26$	$-19 \leq l \leq 18$
Reflections collected	11985	50336	20684
Reflections observed [$I > 2\sigma(I)$]	4750	1207	3482
Max./min. transmission	0.9693/0.9118	0.8769/0.8769	0.8642/0.7050
Data/parameters	1501/82	6273/298	5280/238
Goodness-of-fit on F^2, S	1.021	1.017	1.025
Final *R* indices [$I > 2\sigma(I)$]	0.0405; 0.1067	0.0354; 0.0666	0.0421; 0.1039
R indices (all data)	0.0533; 0.1178	0.0575; 0.0738	0.0771; 0.1243
Largest diff. peak and hole (e Å^{-3})	0.239 and -0.301	0.486 and -0.435	0.540 and -0.124

Crystal structure of rac-,cis-cbpse

Figure 1 depicts the molecular structure of *rac-,cis*-cbpse obtained by oxidation of 1,2-*cis-bis*(phenylsulfide) ethene with 30% H$_2$O$_2$ in HOAc. Selected bond distances and angles with their estimated standard deviations are listed in Table 3. Crystals of the *rac-,cis*-cbpse isomer belong to the *C2/c* space group. The structure of this dissulfoxide shows that the S=O sulfinyl groups are *trans* to each other, and the same is observed for the Ph groups, as seen from the O1–S1–C7–C7#1 and C1–S1–C7–C7#1 torsion angles of 133.7(2)° and $-117.3(2)$°, respectively. The S=O groups are quasi-coplanar with the their bonded Ph rings, as shown by the O1–S1–C2–C6 torsion angle of 7.15(18)º, due to the conjugation between the sulfur lone pairs and the π-systems of the Ph rings. This observation was also previously reported for other phenylsulfinyl derivative.[18]

Crystal structure of [{Ph$_2$SnCl$_2$(meso-bpse)}$_n$]

Figure 2 shows the molecular structure of the adduct [{Ph$_2$SnCl$_2$(*meso*-bpse)}$_n$]. Its structure determination revealed the occurrence of infinite chains along the crystallographic *a* axis; additionally, each *meso*-bpse molecule has an inversion centre at the –H$_2$C–CH$_2$– (ethane) group midpoint. The tin(IV) atom is octahedrally coordinated by Cl atoms at *cis* [Sn–Cl: 2.4591(9), 2.4648(7) Å], by Ph carbon atoms at *trans* [Sn–C: 2.130(3), 2.133(3) Å], and by the two O atoms from the S=O groups at *cis* positions [Sn–O: 2.3527(19), 2.3979(18) Å]. The ligand bonds through both O atoms and forms bridges between the tin(IV) atoms, generating chains along the *n* glide. This kind of chain, along with similar bond distances and angles, has also been observed when Me$_2$SnCl$_2$ replaces Ph$_2$SnCl$_2$. For example, bond distances Sn–C [2.101(4), 2.105(5 Å],
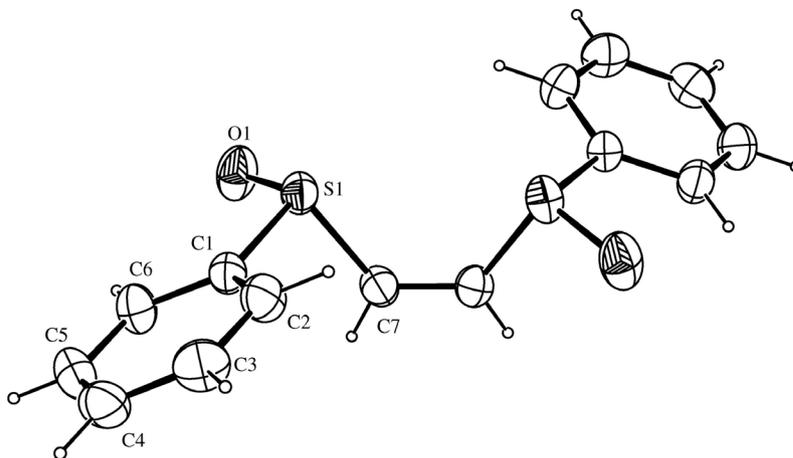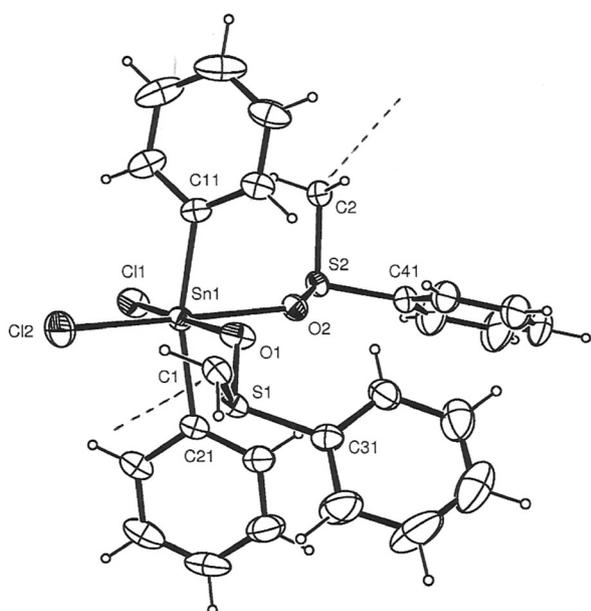
Figure. 1. ORTEP plot of *rac-,cis*-cbpse, with the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Sn–O [2.397(3), 2.404(3) Å], Sn–Cl [2.482(1), 2.486(1) Å] and bond angles Me–Sn–Me [165.2(2)°], O–Sn–O [86.03(1)°] and Cl–Sn–Cl [98.73(4)°] have been observed for [{Me_2SnCl_2(*meso*-bpse)}$_n$].[19]

Crystal structure of [{n-Bu_2SnCl_2(pdtd)}$_2$]

Figure 3 presents the molecular structure of the dimer [{*n*-Bu_2SnCl_2(pdtd)}$_2$]. The X-ray crystal structure revealed a discrete centrosymmetric dimeric assembly in which the tin(IV) atoms possess a distorted octahedral geometry originated from the *bis*-monodentate disulfoxide bonded through the O atoms. One of the *n*-Bu group is disordered (C1a–C4a), while the other group (C5–C8)

does not show any sign of disorder. The dimeric assembly occurs via a 12-membered ring ($Sn_2C_2O_4S_4$) formation and constitutes the first example of a diorganotin(IV) dichloride bonded to a disulfoxide ligand in a 1:1 molar ratio. Usually, most 1:1 adducts of diorganotin(IV) dihalides with disulfoxides form polymeric alternating chains[19–21] containing six-coordinate tin(IV), but 1:1 five-coordinate adducts are rare. In view of this, it is interesting to compare our results with literature data for the five-coordinate adduct [Ph_2SnCl_2(pdtd)].[16] The trigonal bipyramidal structure of the monomer [Ph_2SnCl_2(pdtd)] shows two nearly identical equatorial bond distances Sn–C [2.11(5); 2.122(5) Å] and different axial Sn–Cl [2.455(1) Å] and equatorial Sn–Cl [2.346(2) Å] bond lengths, as

Figure 2. ORTEP plot of [{Ph_2SnCl_2(*meso*-bpse)}$_n$] with the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.
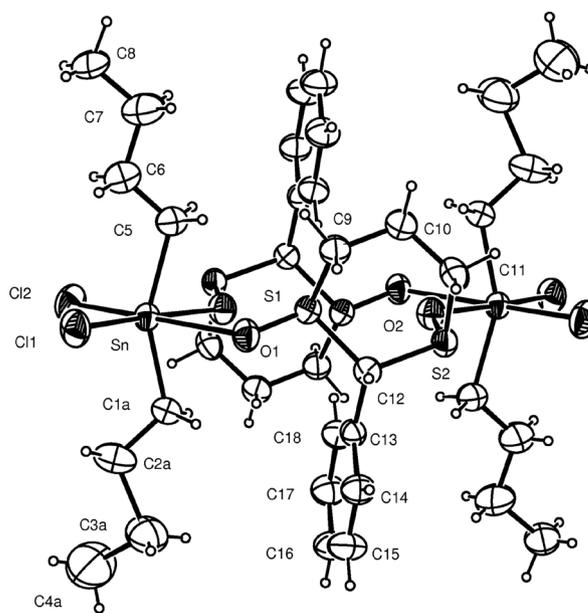
Figure 3. ORTEP plot of [{*n*-Bu_2SnCl_2(pdtd)}$_2$] with the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

expected. The Sn–O distance [2.367(3) Å] is significantly shorter than the similar Sn–O [2.482(3) and 2.755(3) Å] observed for our dimeric adduct, probably due to the more acidic nature of Ph_2SnCl_2 compared to $n\text{-}Bu_2SnCl_2$, whereas the two S=O distances of 1.533(4) and 1.450(6) Å are significantly different, as a consequence of the former being complexed to tin(IV) and the latter remaining uncoordinated. However, in our dimeric adduct the shorter S=O distances of 1.501(3) and 1.512(3) Å indicate that the acid-base interactions are not strong enough. Perhaps, the long Sn–O1# bond distance of 2.755(3) Å is the reason the dimer dissociates in solution to the monomeric form, as suggested by spectroscopic data (Table 1). The values of the 90.35(6)° angle subtended by the two Cl atoms and of the equatorial C–Sn–C bond angle [138.6(2)°] observed in [Ph_2SnCl_2(pdtd)] are smaller than the equivalent angles found in our octahedral adduct, as expected (Table 3).

Table 3. Selected bond lengths (Å) and angles (°) for *rac-,cis-*cbpse and tin(IV) adducts

*rac-,cis-*cbpse			
C1–S1	1.7992(17)	C1–S1–C7	95.56(8)
O1–S1	1.4829(15)	C1–S1–O1	106.79(8)
C7–S1	1.7889(17)	C7–S1–O1	104.62(9)
C7–C7#	1.316(3)	S1–C7–C7#	124.41(5)
[{Ph_2SnCl_2(*meso*-bpse)}$_n$]			
Sn1–C11	2.133(3)	C11–Sn1–C21	163.79(11)
Sn1–C21	2.130(3)	Cl1–Sn1–O1	176.19(6)
Sn1–Cl1	2.4648(7)	Cl2–Sn–O2	173.41(6)
Sn1–Cl2	2.4591(9)	C11–S1–Cl2	94.49(4)
Sn1–O1	2.3979(18)	O1–Sn1–O2	84.33(7)
Sn1–O2	2.3527(19)	C11–Sn1–O2	91.90(5)
S1–O1	1.514(2)	Cl2–Sn–O1	89.30(6)
S1–O2	1.520(2)	O1–S1–C1	104.49(13)
C1–C2#1	1.520(4)	O2–S1–C2	103.48(12)
[{$n\text{-}Bu_2SnCl_2$(pdtd)}$_2$]			
Sn–C1a	2.07(7)	C1a–Sn–C5	153.1(17)
Sn–C5	2.132(5)	C1a–Sn–O2#1	80.2(15)
Sn–O2	2.483(3)	C1–Sn–Cl2	100.3(15)
Sn–O1#1	2.755(3)	Cl1–Sn–O2#1	174.89(8)
Sn–Cl1	2.4535(11)	C5–Sn–Cl2	100.31(15)
Sn–Cl2	2.4175(13)	Cl1–Sn–Cl2	97.96(5)
C9–S1	1.797(4)	C5–Sn–O2#1	83.68(16)
S1–O1	1.501(3)	C9–S1–O1	106.70(19)
S2–O2	1.511(3)	S2–O2–Sn#1	129.25(16)
C11–S2	1.798(4)	C6–C5–Sn	117.8(4)
C12–S2	1.821(4)	C11–S2–O2	104.9(2)
C9–C10	1.535(7)	C9–C10–C11	113.4(8)

Structure of [{Ph_2SnCl_2·(rac-,cis-cbpse)}$_x$] (x = 2 or n)

The spectroscopic data shown in Table 1 indicate that [{Ph_2SnCl_2(*rac-,cis*-cbpse)}$_x$] do not show any evidence of a monomeric adduct in which the tin(IV) atoms exhibit trigonal bipyramidal geometry in the solid state. However, the same spectroscopic data are not sufficient to characterize the product as being a dimeric [{Ph_2SnCl_2(*rac-, cis*-cbpse)}$_2$], or a polymeric [{Ph_2SnCl_2(*rac-,cis*-cbpse)}$_n$] compound containing octahedral tin(IV) centres.

Conclusions

The reaction between Ph_2SnCl_2 and the disulfoxide pdtd in 1:1 molar ratio affords a monomeric[16] adduct containing a five-coordinate tin(IV) centre, while a similar reaction with $n\text{-}Bu_2SnCl_2$ affords dimeric species in which the tin(IV) atoms are six-coordinate. Surprisingly, the characterization of the adduct [{Ph_2SnCl_2(*rac-,cis*-cbpse)}$_x$] as being a dimeric or a polymeric species was not possible using microanalysis and spectroscopic methods such as IR, NMR and [119]Sn Mössbauer.

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Supplementary Information

Crystallographic data for the compounds have been deposited at the Cambridge Crystallographic Data Center with the deposition numbers CCDC 694402 for *rac-,cis-*cbpse, CCDC 679894 for [{Ph_2SnCl_2(*meso*-bpse)}$_n$] and CCDC 693796 for [{$n\text{-}Bu_2SnCl_2$(pdtd)}$_2$]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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