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Article

Adduct Formation Between Diphenyltin Dichloride and 2-phenyl-1,3-dithiane *trans*-1-*trans*-3-dioxide. Preparation, Spectroscopy, Crystal and Molecular Structure of $[Ph_2SnCl_2.CH_2(CH_2)_2SOCH(Ph)SO]$

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Um novo aduto pentacoordenado de Sn (IV) foi preparado a partir de dicloreto de difenilestanho (IV) e do dissulfóxido 2-fenil-1,3-ditiano *trans-1*,*trans-3*-dióxido. O estudo espectroscópico e por difração de raios-X mostrou ser o novo composto um exemplo raro de aduto pentacoordenado 1:1 entre uma espécie organometálica de Sn (IV) e um ligante neutro. Apesar de ser difuncional, o ligante apresenta-se monodentado, em virtude de sua geometria peculiar. Ademais, o aduto não mostra evidência de interação intermolecular forte, formando moléculas discretas.

A new pentacoordinate Sn (IV) adduct was prepared from diphenyltin (IV) dichloride and the disulphoxide 2-phenyl-1,3-dithiane *trans-1*, *trans-3*-dioxide. Spectroscopic and X-ray diffraction studies showed the new compound to be a rare example of a pentacoordinate 1:1 adduct between an organometallic Sn (IV) species and a neutral ligand. In spite of being difunctional, the ligand is monodentate as a result of its peculiar geometry. Moreover, the adduct does not show any evidence of strong intermolecular interactions, forming discrete molecules.

Keywords: *Sn (IV) adduct, tin organometallics, tin-disulphoxide adduct*

Introduction

Most 1:1 adducts of diorganotin (IV) dihalides with Lewis donor ligands are actually six-coordinate dimeric species, in particular when the organic group is methyl[1]. Only a few adducts of this type are truly pentacoordinate[2], such as that formed between diphenyltin (IV) dichloride with benzothiazole[2], and those between both diphenyltin (IV) dichloride and trimethyltin (IV) chloride with 2,6-dimethylpyridine[3], as well as that which occurs between dimethyltin (IV) dichloride and dibenzylsulphoxide[4]. A curious example is given by the pyrazine adducts with dimethyltin (IV) dichloride and diphenyltin (IV) dichloride. Both cases produce polymeric chains in which the ligand and the organotin moiety alternate. The first of these adducts has a structure made up exclusively of six-coordinate tin atoms in the chains. The second, however, forms alternating chains containing five- and six-coordinate tin centres, respectively[5].

We report here the preparation and the spectroscopic and structural study of a true pentacoordinate adduct in-

volving diphenyltin (IV) dichloride and the disulphoxide 2-phenyl-1,3-dithiane *trans-1, trans-3*-dioxide, $[CH_2(CH_2)_2SOCH(Ph)SO]$.

Of the two SO functional groups only one formed a bond with the Sn atom, and no appreciable intermolecular interaction was observed between individual adduct molecules.

Experimental

The ligand was kindly provided by Prof. C. Celso, who had previously synthesised it.

Equal amounts (1.45 m mole) of both Ph_2SnCl_2 and the ligand were dissolved in 10 mL of dry EtOH. After refluxing for 2 h, the mixture was filtered, and a clear solution obtained. Slow cooling and evaporation of this solution yielded an abundant crop of needle-like colourless crystals. These were filtered off and washed with ether. The yield of pure product was 0.60 g (72%), and the adduct decomposed at 177 °C. An attempt to prepare a 2:1 adduct using a large excess of ligand was unsuccessful. C, H analysis of the product gave C, 46.02; H, 3.82%; calculated for $C_{22}H_{22}O_2S_2Cl_2Sn$ gives C, 46.18; H, 3.85%.

I. R. spectra were recorded from a 283 B Perkin-Elmer instrument using CsI pellets. Mössbauer spectra were obtained from a constant acceleration spectrometer moving a $CaSnO_3$ source at room temperature. Samples were analysed at 85 K with respect to that source. ^{119}Sn NMR spectra were run in $CDCl_3$ in a 250 MHz Bruker instrument, using Me_4Sn as a reference. The molecular structure of the adduct was established by a single crystal diffraction study using an Enraf-Nonius CAD-4 diffractometer.

Crystal data for $C_{22}H_{22}O_2S_2Cl_2Sn$: M = 572.1, monoclinic space group $P2_1/c$, cell dimensions, a = 15.126 (1), b = 9.603 (1), c = 16.270 (3) Å; β = 101.82 (1)º, V = 2313.1 Å^3, Z = 4, D_{calc} = 1.64 g cm^{-3}. Monochromated Mo Kα radiation λ = 0.71069 Å, μ = 15.3 cm^{-1}. The structure of the crystal (0.1 x 0.1 x 0.05 mm) was solved by routine heavy atom techniques and refined by full-matrix least-squares methods with non-H atoms anisotropic, using Enraf-Nonius SDP programs. 2949 significant reflections with $|F^2| > 2\sigma(F^2)$ were used in the refinement, which converged at R = 0.039 and R'= 0.049.

Results and Discussion

Table 1 presents spectroscopic data for our adduct as well as for its precursors. The I.R. spectrum of the ligand shows only one SO band at 1044 cm^{-1}, which in the adduct appears at 1044 and 950 cm^{-1}, indicating two different SO groups. This is consistent with the fact that one SO function is bonded to the metal, causing the shift to lower frequency (950 cm^{-1}), whereas the other SO group remains uncomplexed, which accounts for its practically unchanged frequency. The I.R. spectrum also shows a band at 420 cm^{-1}, which we assigned to the SnO vibration[6]. The SnCl bands were shifted to lower frequencies compared to the precursor Ph_2SnCl_2, which is characteristic of adducts of organotin halides[6].

The ^{119}Sn NMR spectrum in $CDCl_3$ showed a single absorption at δ -62, upfield from Ph_2SnCl_2, due to enhanced shielding of the Sn nucleus in the adduct[7], compared to the precursor (δ -33).

The ^{119}Sn Mössbauer spectrum of the adduct showed an increase in the quadrupole splitting and no variation in the isomer shift, compared to Ph_2SnCl_2. The increase in the quadrupole splitting may be accounted for by a greater asymmetry in the electronic density distribution around the Sn nucleus, whereas the invariance in δ is surprising. An expansion in the coordination number of tin upon adduct formation usually tends to produce lower δ values as a consequence of rehybridisation and less s orbital participation in the overall hybrid orbitals[8]. Of course δ values do not depend only on the hybridisation of tin, but also on the total charge distribution, *i.e.*, on the polarisation of the bonds. The two effects may have acted here to balance each other out, leading to the same value of δ in both the precursor and the adduct.

Figure 1 shows the molecular structure of the adduct and Fig. 2 the corresponding unit cell. Table 2 presents the most important bond distances and angles, as well as some of the dihedral angles of the adduct.

Figure 1 shows the adduct as a pentacoordinate trigonal bipyramidal species, and Fig. 2 shows the arrangement of the individual molecules in their unit cell. The monomeric character of the adduct is shown by the fact that the Sn-Cl'(1) distance, between the Sn atom of a given molecule

Table 1. Spectroscopic Data.

Compound	I.R. absorptions (cm^{-1})			^{119} Sn n.m.r. (δ)	^{119}Sn Mössbauer (mms^{-1})	
	ν_{SO}	ν_{SnCl}	ν_{SnO}		δ	Δ
Ligand	1044					
Ph_2SnCl_2		364, 356[a]		-33	1.32	2.85
adduct	1040, 950	295, 240	420	-62	1.32	3.22

[a] Ref. 9.

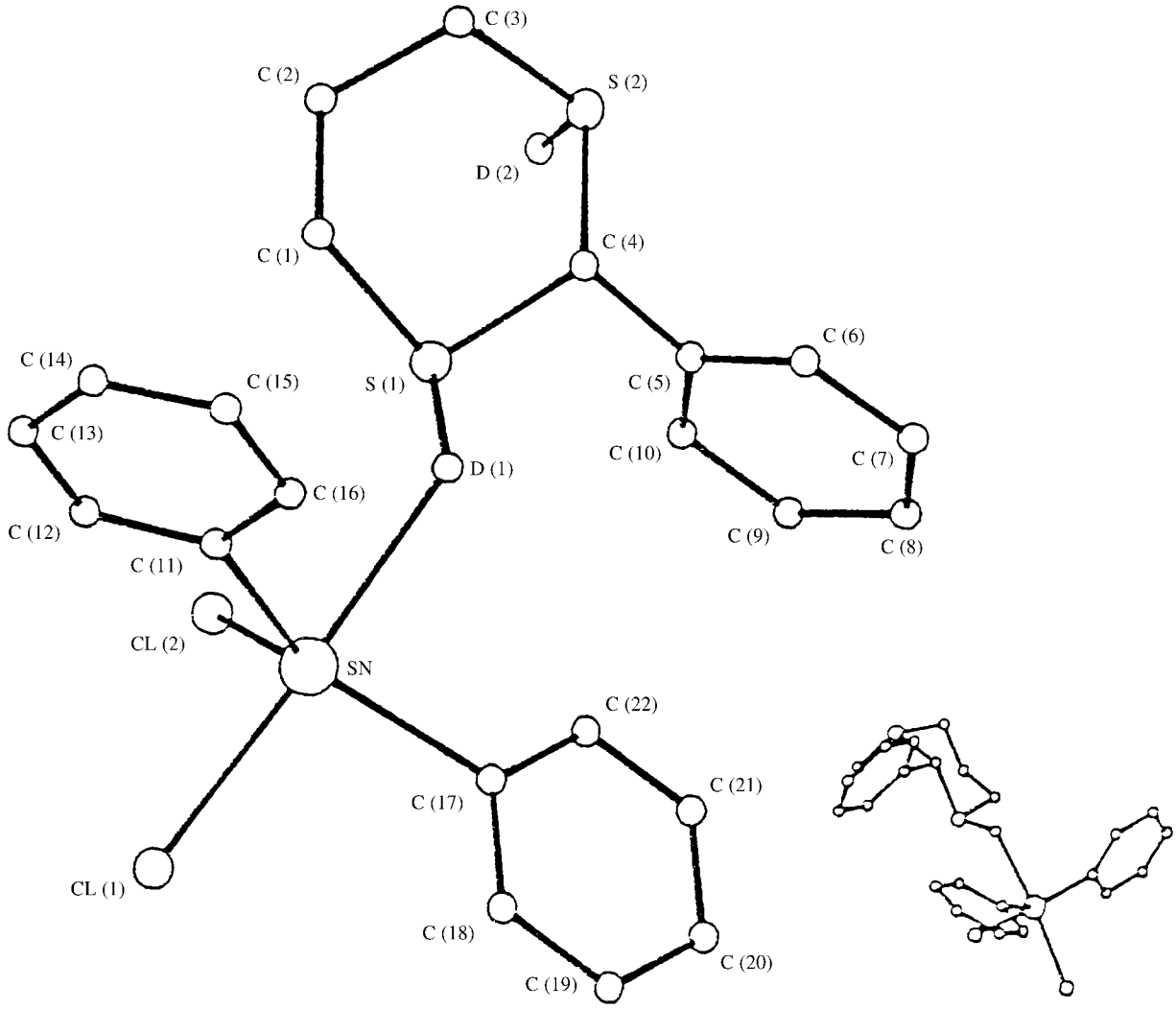

Figure 1. The molecular structure of the adduct $[Ph_2SnCl_2.CH_2(CH_2)_2\ SO(Ph)SO]$

and the axial Cl' atom of its nearest neighbour was found to be 4.29 Å, greater than the sum of the van der Waals radii of Sn (2.20 Å) and Cl (1.70-1.90 Å)[10]. Figure 2 clearly shows that the self-association so common in organotin compounds is not present in this case, and the complex is indeed pentacoordinate.

The trigonal bipyramidal stucture of the monomer shows two nearly identical equatorial Sn-C bonds and a longer Sn-Cl (2) bond, as expected. The equatorial angles are 108.8 (2)º and 110.2 (1)º for Cl (2)-Sn-C (11) and Cl (2)-Sn-C (17), respectively, whereas the C (11)-Sn-C (17) angle is 138.6 (2)º. The axial angle Cl (1)-Sn-O (1) is 173.1 (1)º, showing a small deviation from a regular trigonal bipyramidal angle of 180º. The Sn-O (1) distance is 2.367 (3) Å, and the two S-O distances are significantly different: S(1)-O (1) is 1.533 (4) Å, whereas S (2)-O (2) is 1.450 (6) Å, as a consequence of the former being complexed to Sn, and the latter remaining nonbonded.

It is interesting to compare our results with literature data for the similar pentacoordinate adduct $[Me_2SnCl_2.O{=}S(CH_2Ph)_2]$[4]. In the latter complex the two equatorial Cl-Sn-C angles are 108.2 (6) and 113.0 (6)º, respectively, and the equatorial C-Sn-C angle is 136.4 (19)º. The axial Cl-Sn-O angle is 173.9 (4)º, and the Sn-O and S-O distances are 2.319 (10) and 1.488 (21) Å, respectively.

The two equatorial phenyl groups in our complex are almost perpendicular to each other; indeed their dihedral angle is 87.35º. The equatorial phenyl group represented by atoms C (17) to C (22) and the phenyl group of the ligand [C (5) to C (10)] form a dihedral angle of 84.04º. In contrast, the phenyl group of the ligand and the second equatorial phenyl ring [C (11) to C (16)] are almost parallel, with a dihedral angle of only 7.00º between them.

Additional crystallographic data can be obtained from the authors on request.

Table 2. X-Ray Diffraction Data for the Adduct [$Ph_2SnCl_2.CH_2(CH_2)_2SOCH(Ph)SO$].

Intermolecular distances (Å)		Bond Angles (º)		Dihedral Angles (º)	
Sn - Cl (1)	2.455 (1)	Cl (1) - Sn - Cl (2)	90.35 (6)	Planes 1-2	87.35 ± 0.18
Sn - Cl (2)	2.374 (2)	Cl (1) - Sn - C (11)	97.2 (1)	Planes 1-3	7.00 ± 1.44
Sn - O (1)	2.367 (3)	Cl (1) - Sn - O (1)	173.1 (1)	Planes 2-3	84.04 ± 0.18
Sn - C (11)	2.118 (5)	Cl (2) - Sn - O (1)	82.8 (1)		
Sn - C (17)	2.122 (5)	Sn - O (1) - S (1)	128.5 (2)		
S (1) - O (1)	1.533 (4)	Cl (1) - Sn - C (17)	96.0 (1)		
S (2) - O (2)	1.450 (6)	Cl (2) - Sn - C (11)	108.8 (2)		
		Cl (2) - Sn - C (17)	110.2 (1)		
		O (1) - Sn - C (11)	84.3 (2)		
		O (1) - Sn - C (17)	87.2 (2)		
		C (11) - Sn - C (17)	138.6 (2)		
		O (11) - S (1) - C (1)	105.0 (3)		
		O (1) - S (1) - C (4)	99.1 (3)		
		O (2) - S (2) - C (3)	108.4 (3)		
		O (2) - S (2) - C (4)	107.9 (3)		

a Plane 1: C (11) C (12) C (13) C (14) C (15) C (16). Plane 2: C (17) C (18) C (19) C (20) C (21) C (22). Plane 3: C (5) C (6) C (7) C (8) C(9) C (10).

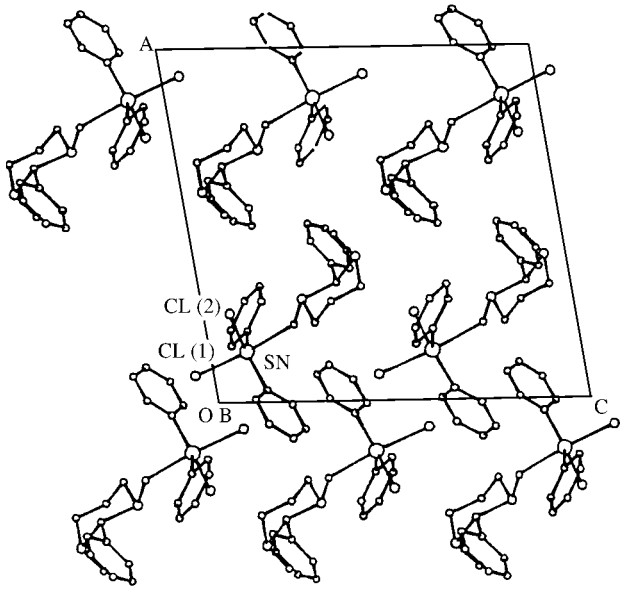

Figure 2. The unit cell of the adduct [$Ph_2SnCl_2.CH_2(CH_2)_2SOCH(Ph)SO$]

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