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Comparative stereochemical studies of Ph_3SnL complexes (L = 1-carbodithioato vs. 1-carbothioato ligand). Crystal structures of $[Ph_3Sn(S.CS.N(CH_2)_5]$ and $[Ph_3Sn(S.CO.N(CH_2)_4O)]$

Shubhra Chandra, Bruce D. James, Robert J. Magee,
Department of Chemistry, La Trobe University, Bundoora, Vic., 3083 (Australia)

Wyona C. Patalinghug, Brian W. Skelton and Allan H. White
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia, 6009 (Australia)

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Abstract

Single crystal X-ray structure determinations have been carried out on $[Ph_3Sn(S.CS.N(CH_2)_5)]$ (**1**) and $[Ph_3Sn(S.CO.N(CH_2)_4O)]$ (**2**) (the latter the first organotin(IV) complex of the monothiocarbamate ligand) and the results compared with those recently reported for $[Ph_3Sn(S.CS.N(CH_2)_4)]$ (**3**) in order to throw light on details of the variations in the Sn environment and their possible causes. The crystals of compounds **1** and **2** are monoclinic, $P2_1/c$, $Z = 4$. For **1** a 10.009(5), b 15.959(7), c 15.831(6) Å, β 115.79(3)°; R was 0.026 for $N_o = 2224$ 'observed' reflections. For **2**, a 15.16(1), b 9.560(7), c 18.47(2) Å, β 125.06(5)°; $R = 0.031$ for $N_o = 2642$. The overall molecular structures are similar, and similar to those of **3**, with wide but parallel variations in C–Sn–C (~ 102–120°) and S–Sn–C angles (~ 91–120°). In **1** the Sn–S bond lengths are 2.481(2), 2.919(2) Å, while in **2** the Sn–S,O bond lengths are 2.446(2), 2.809(4) Å, the longer distances in each case being associated with considerable double bond character in the adjacent C–S,O linkage (1.678(4), 1.243(6) Å).

Introduction

In a recent paper trends in coordination number and dithiocarbamate ($dtc^- \equiv R_2NCS_2^-$) ligand coordination mode were systematically examined in complexes of the type $R_mSn(dtc)_n$ as a function of the $m:n$ stoichiometry [1]. In particular, for derivatives of the type Ph_3Sndtc, the complexes contain essentially four-coordinate

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tin, but with wide variations from the normal tetrahedral environment that are unrelated to 'an electronegativity difference between the sulfur and phenyl groups'; the dithiocarbamate ligands are essentially monodentate. In this context, it is of interest to record and compare results we have obtained on two similar systems, namely $Ph_3Sn(S_2CN(CH_2)_5)$ (**1**) the next homologue of the tetramethylene derivative recorded in ref. 1 and $Ph_3Sn(S.CO.N(CH_2)_4O)$ (**2**) [2], the first monothiocarbamate organotin(IV) derivative to be structurally characterised.

Results and discussion

Non-hydrogen atom coordinates for **1** and **2** are given in Table 1, and details of the tin environments are shown in Table 2, along with data for the previously described $S_2CN(CH_2)_4$ analogue, **3**; for both **1** and **2**, the asymmetric unit is a single discrete molecule of the expected stoichiometry. (For purposes of comparison

Table 1

Non-hydrogen atom coordinates

Atom	**1**			**2**		
	x	*y*	*z*	*x*	*y*	*z*
Sn	0.79432(3)	0.7287(2)	0.05719(2)	0.76305(2)	0.47051(3)	0.17572(2)
(Di)-thiocarbamate ligand						
S(1)	0.66356(13)	0.60116(7)	0.07100(8)	0.89102(10)	0.32683(14)	0.30391(9)
S,O(2)	0.93558(14)	0.64536(8)	0.23908(8)	0.9795(2)	0.5522(3)	0.2914(2)
C(1)	0.7924(5)	0.5795(3)	0.1862(3)	0.9959(4)	0.4502(5)	0.3394(3)
N	0.7712(4)	0.5111(2)	0.2275(2)	1.0885(3)	0.4308(4)	0.4185(2)
C(2)	0.6377(6)	0.4581(3)	0.1879(3)	1.1151(4)	0.3101(5)	0.4748(3)
C(3)	0.5504(6)	0.4670(4)	0.2438(4)	1.1570(4)	0.3577(6)	0.5673(3)
C,O(4)	0.6474(6)	0.4478(4)	0.3476(4)	1.2440(3)	0.4518(4)	0.6013(2)
C(5)	0.7860(6)	0.4987(3)	0.3844(3)	1.2124(4)	0.5715(6)	0.5458(4)
C(6)	0.8680(5)	0.4890(3)	0.3255(3)	1.1747(4)	0.5324(6)	0.4533(3)
Phenyl ligands						
C(*a*1)	0.6209(4)	0.7541(2)	−0.0818(3)	0.6226(3)	0.3534(5)	0.1402(3)
C(*a*2)	0.4770(5)	0.7696(3)	−0.0944(3)	0.5973(4)	0.3422(5)	0.2009(3)
C(*a*3)	0.3629(5)	0.7839(3)	−0.1826(3)	0.5123(4)	0.2590(6)	0.1844(4)
C(*a*4)	0.3902(5)	0.7835(3)	−0.2602(3)	0.4519(4)	0.1871(6)	0.1057(4)
C(*a*5)	0.5319(5)	0.7691(3)	−0.2499(3)	0.4753(4)	0.1966(6)	0.0450(3)
C(*a*6)	0.6482(5)	0.7538(3)	−0.1611(3)	0.5599(4)	0.2801(5)	0.0619(3)
C(*b*1)	0.7938(4)	0.8423(3)	0.1305(3)	0.7401(3)	0.6822(5)	0.1968(3)
C(*b*2)	0.7119(5)	0.9092(3)	0.0777(3)	0.6465(4)	0.7214(5)	0.1889(3)
C(*b*3)	0.7046(5)	0.9844(3)	0.1194(3)	0.6270(4)	0.8617(5)	0.1949(3)
C(*b*4)	0.7800(5)	0.9929(3)	0.2152(3)	0.6995(4)	0.9628(5)	0.2091(3)
C(*b*5)	0.8606(6)	0.9282(3)	0.2682(3)	0.7925(4)	0.9264(5)	0.2182(3)
C(*b*6)	0.8701(5)	0.8533(3)	0.2273(3)	0.8128(4)	0.7870(5)	0.2119(3)
C(*c*1)	0.9829(4)	0.6979(3)	0.0337(3)	0.7935(3)	0.4516(5)	0.0772(3)
C(*c*2)	1.0431(5)	0.7572(3)	−0.0039(3)	0.7119(4)	0.4819(5)	−0.0110(3)
C(*c*3)	1.1596(5)	0.7367(3)	−0.0252(3)	0.7308(4)	0.4748(6)	−0.0762(3)
C(*c*4)	1.2160(5)	0.6572(4)	−0.0110(3)	0.8299(5)	0.4404(6)	−0.0549(4)
C(*c*5)	1.1583(5)	0.5982(3)	0.0263(3)	0.9116(4)	0.4110(6)	0.0314(4)
C(*c*6)	1.0426(5)	0.6178(3)	0.0482(3)	0.8939(4)	0.4167(5)	0.0971(3)

Table 2

The tin and dithiocarbamate geometries

	[Ph$_3$Sn(S$_2$CN(CH$_2$)$_5$] **(1)**	[Ph$_3$Sn(S.CO.CN(CH$_2$)$_4$O)] **(2)**	[Ph$_3$Sn(S$_2$CN(CH$_2$)$_4$] [a] **(3)**
Distances (Å)			
Sn–C(*a*1)	2.167(3)	2.149(5)	2.167(10)
Sn–C(*b*1)	2.154(4)	2.127(5)	2.155(10)
Sn–C(*c*1)	2.134(5)	2.127(6)	2.124(10)
Sn–S(1)	2.481(2)	2.446(2)	2.468(3)
Sn–O,S(2)	2.919(2)	2.809(4)	3.106(3)
C(1)–S(1)	1.750(4)	1.775(5)	1.776(11)
C(1)–O, S(2)	1.678(4)	1.243(6)	1.702(11)
C(1)–N	1.336(6)	1.336(5)	1.267(14)
Angles (degrees)			
C(*a*1)–Sn–C(*b*1)	101.6(1)	108.3(2)	103.9(4)
C(*a*1)–Sn–C(*c*1)	104.1(2)	111.0(2)	107.8(4)
C(*b*1)–Sn–C(c1)	119.8(2)	112.1(2)	117.3(2)
C(*a*1)–Sn–S(1)	91.3(1)	95.7(1)	95.0(1)
C(*b*1)–Sn–S(1)	121.2(1)	118.7(1)	119.1(3)
C(*c*1)–Sn–S(1)	111.5(1)	109.8(1)	110.2(3)
C(*a*1)–Sn–O,S(2)	156.5(1)	153.8(1)	157.3(3)
C(*b*1)–Sn–O,S(2)	88.0(1)	80.7(1)	82.0(3)
C(*c*1)–Sn–O,S(2)	88.9(1)	86.6(1)	87.9(3)
S(1)–Sn–O,S(2)	65.59(4)	59.28(9)	63.6(1)
Sn–S,O(2)–C(1)	81.4(1)	89.5(3)	79.2(4)
Sn–S(1)–C(1)	94.4(2)	91.6(2)	98.6(4)
S(1)–C(1)–N	118.0(3)	119.2(3)	116.7(8)
S(1)–C(1)–O,S(2)	118.6(3)	117.8(4)	118.3(6)
N–C(1)–O,S(2)	123.4(3)	122.9(4)	124.9(8)
C(1)–N–C(2)	124.7(3)	125.6(4)	126.2(10)
C(1)–N–C(5,6)	122.7(3)	120.3(4)	122.3(10)
C(2)–N–C(5,6)	111.7(4)	114.1(3)	111.6(10)

[a] Atoms relabelled to match the scheme used for **1** and **2** (Fig. 1).

we note that in tetraphenyltin(IV), Sn–C is 2.143(5) Å, with C–Sn–C 108.9(2), 110.5(2)° [3]). The following features are noted:

(*1*) In both **1** and **2** the (di-) thiocarbamate ligand is essentially monodentate; S.C(O, S).N is essentially planar, χ^2 0.1(1), 5.9(2)) with tin deviations of 0.059, 0.305 Å.

(*2*) The disposition of the three phenyl groups with respect to the sulphur ligand is similar in both compounds (Fig. 1) and to that in **3**, with the pendant carbon of ring *a* pseudocoplanar with the sulphur ligand and the tin, and rings *b*, *c* disposed to either side; C(*a*1) lies adjacent to the coordinated sulfur atom.

(*3*) The C–Sn–C angles about tin, show gross and parallel deviations from the tetrahedral value in **1** and **3**, but in **2** these are much smaller. The mean Sn–C bond lengths in **1** and **3** are 2.15$_2$, 2.15$_2$ Å, perhaps slightly larger than in tetraphenyltin(IV), while in **2**, the value is 2.13$_4$ Å, perhaps slightly less, and certainly shorter than in **1** and **3**. Overall the C$_3$Sn geometry in **2** is suggestive of a closer approach to a four-coordinate tetrahedral norm than is the case with **1** and **3**.

(*4*) The Sn–S(1)–C(1) geometry suggests that the Sn–S bond is stronger in **2** than in **1**; the highly localized C=O double bond is compatible with this feature, which, it

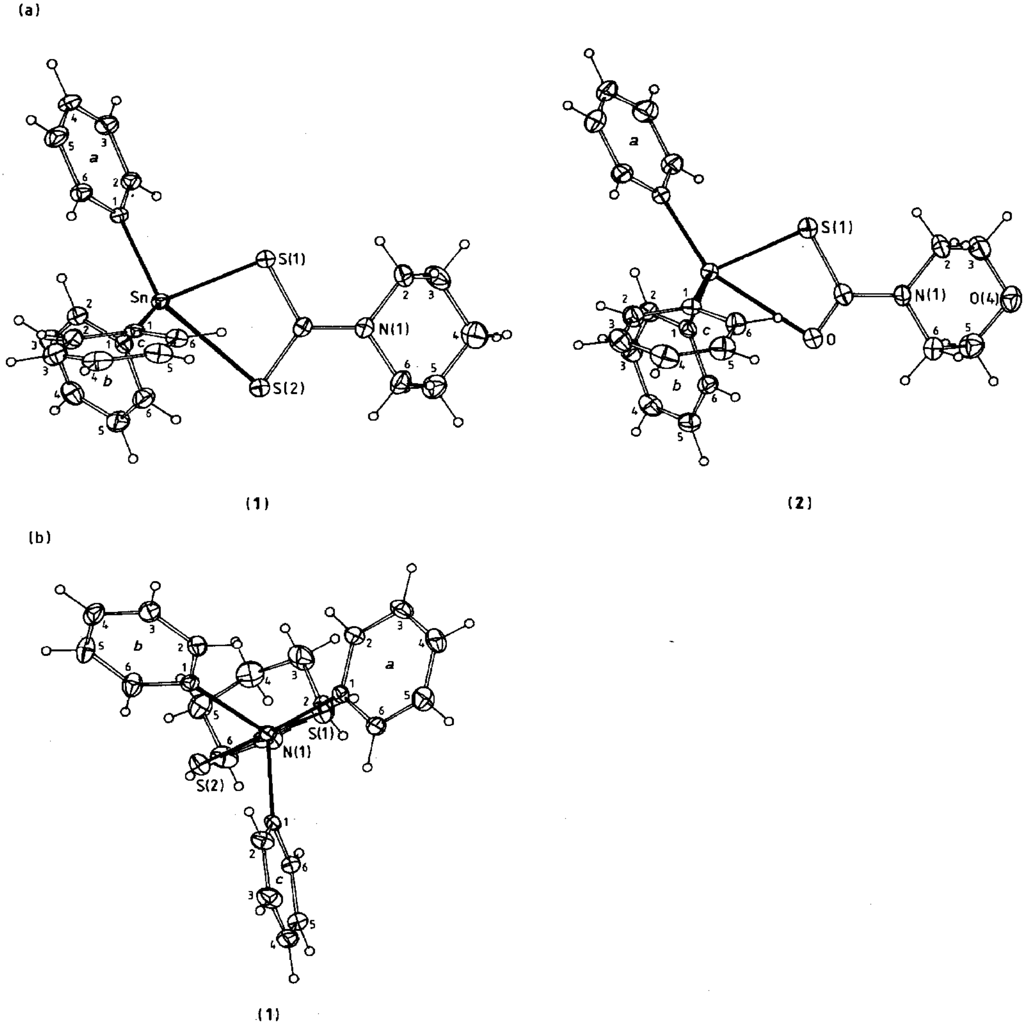

Fig. 1. Projections of **1** and **2**; (a) normal to the sulphur ligand plane; (b) **1** down the pseudo-threefold C_3Sn axis. 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have an arbitrary radius of 0.1 Å.

is interesting to note, is not reflected in a change in the associated C–N distance. In **3**, elongation of both C–S distances is consistent with an unusually short $C-N(CH_2)_4$ distance, and also with an Sn–S(1) distance intermediate between the values for **1** and **2**. It is also unusual to observe a metal–sulphur distance for the $S_2CN(CH_2)_4$ ligand (a weak crystal field ligand, at least in the context of transition metal complex chemistry) that is shorter than the value for the (stronger field) $S_2CN(CH_2)_5$ ligand, and this may reflect the above changes in ligand delocalization consequent upon the change from a bi- to essentially mono-dentate ligand. Notwithstanding the latter comment, it is of interest to note the substantially shorter Sn–S(2) distance in **1** vis-à-vis.**3**, in keeping with the difference in C–S(2) distances, with S(1)–C–S(2) identical.

Table 3

Ligand torsion angles

Six-membered ring torsion angles are given for **1** and **2**, and for comparison, the corresponding values for $(S.CS.N(CH_2)_5)_2$ and $[Ni(S_2CN(CH_2)_4O)_2]$ [5,6]. Carbon atoms are defined by number only; **4** may be O

Atoms	**1**	**2**	$(S.CS.N(CH_2)_5)_2$	$[Ni(S_2CN(CH_2)_4O)_2]$
1–N–2–3	−110.6	−130.3	−112.2, −108.0	−141.1
6–N–2–3	59.3	52.3	60.9, 61.7	49.0
N–2–3–**4**	−55.2	−54.3	−56.1, −54.6	−54.3
2–3–**4**–5	52.9	58.6	51.7, 50.8	61.7
3–**4**–5–6	−53.5	−59.4	−51.7, 51.6	−61.9
4–5–6–N	56.4	55.5	55.0, 56.1	55.2
5–6–N–2	−59.2	−53.0	−59.6, −62.3	−49.5
5–6–N–1	110.8	129.4	113.1, 107.1	140.6

(*5*) The proximity of the strongly bound S(1) to C(*a*1), with an S(1)–Sn–C(*a*1) angle nearer a right angle rather than to a tetrahedral angle in all cases, is reflected only in a very slight (and possibly not significant) elongation of Sn–C(*a*1) relative to Sn–C(*b*, *c*1) in all the compounds. The consistent types of distortion in the angular geometry about the tin may well arise from the splayed disposition of ring *b*, *c* relative to the planar sulphur ligand with short *ortho*-hydrogen contacts to O, S(2) (H(6, *c*6) $\cdots$ S(2), 2.6_3, 3.1_7 Å in **1**; H(*b*6) $\cdots$ O, 2.4_1 Å in **2**).

(*6*) In spite of similar ring sizes, a curious discrepancy is found in the angles between the pair of substituent atoms at the nitrogen, that for the piperidyl ring being appreciably less than that in the morpholyl (111.7(4) vs. 114.1(3)°); this is mirrored in similar structures containing these moieties, e.g. in $(S.CS.N(CH_2)_5)_2$ and $[Ni(S_2CN(CH_2)_4O)_2]$, the angles are (111.8, 112.0(3)) and 114.8(2)°, [5,6], presumably as a consequence of shortened C,4(O)-adjacent atom distances since there is at most only a slight difference in the angles at C(4) or O(4) (or their counterparts in these related structures); those in the piperidine rings are 111.0(5), (**1**), 111.1(3), 112.0(3)° and those in the morpholine rings 110.5(4), (**2**), 109.6(2)°. Particularly evident is the difference found in the dihedral angles for the two ring types (Table 3), to either side of the nitrogen and atom 4.

Experimental

Triphenyltin chloride was obtained from Aldrich Chemical Co. and used without further purification. The mono- and di-thiocarbamate derivatives were prepared from the triphenyltin chloride in acetone by previously described methods [2,4]. Crystals suitable for X-ray determination were obtained by slow evaporation of acetone solutions, containing ca. 5% of water.

Structure determination

Unique data sets were measured at 295 K up to $2\theta_{max} = 50°$ on a Syntex $P2_1$ four-circle diffractometer used in the conventional $2\theta/\theta$ scan mode (monochromatic Mo-K_α radiation source, λ 0.7106_9 Å). N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered "observed' and used in the full matrix least squares refinement after Gaussian absorption correction and solution of the structures by vector methods. Anisotropic thermal parameters were used for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Residuals on $|F|$ at convergence, R, R' (statistical weights derived from $\sigma^2(I) = \sigma^2(I)_{diff} + 0.0000n\ \sigma^4(I)_{diff}$) are quoted. Neutral complex scattering factors were used; for computations the XTAL program system was used, and implemented by S.R. Hall using a Perkin–Elmer 3240 computer [7,8].

Crystal data

(**1**) $C_{24}H_{25}NS_2Sn$, $M = 510.3$, Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a 10.009(5), b 15.959(7), c 15.831(6) Å, β 115.79(3)°, U 2277(2) Å^3. $D_c(Z = 4)$ 1.50 g cm^{-3}. $F(000) = 1032$. μ_{Mo} 13.1 cm^{-1}; Specimen: $0.10 \times 0.27 \times 0.10$ mm, $A^{\star}_{min,max} = 1.09, 1.12$. $N = 2994$, $N_o = 2224$, $R = 0.026$, $R' = 0.022$ ($n = 6$).

(**2**) $C_{23}H_{23}NO_2SSn$, $M = 496.2$, Monoclinic, space group $P2_1/c$, a 15.16(1), b 9.560(7), c 18.47(2) Å, β 125.06(5)°, U 2192(3) Å^3. $D_c(Z = 4)$ 1.50 g cm.$^{-3}$. $F(000) = 1000$. μ_{Mo} 12.0 cm^{-1}; Specimen $0.13 \times 0.46 \times 0.05$ mm, $A^{\star}_{min,max} = 1.06, 1.20$. $N = 3652$, $N_o = 2642$. $R = 0.031$, $R' = 0.028$ ($n = 4$).

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