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Crystal and molecular structure of 1-phenyl-1*H*-tetrazole-5-thiolato-trimethyltin(IV), Me_3SnSCN_4Ph, exhibiting unusual trimeric associations through intermolecular N → Sn bonds

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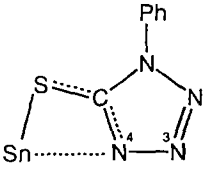
Abstract

The title compound is rhombohedral, space group $R3$, with $a = 18.097(4)$, $c = 10.832(5)$ Å, $Z = 9$, $D_c = 1.658$ g cm^{-3}. The crystal contains trimeric $[Me_3SnSCN_4Ph]_3$ units in which the heterocyclic ligand is bridging two metal atoms (Sn(1)–S(1) 2.565(4) Å, N(3) → Sn(1a) 2.747(14) Å). Additionally, weak intramolecular Sn(1) · · · N(4) secondary bonds of 3.285(12) Å are also present, thus leading to a bimetallic triconnective coordination pattern of the ligand.

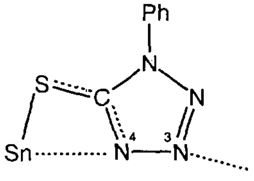
Keywords: Tin; Tetrazoles

1. Introduction

Several Main Group organometallic complexes of 1-phenyl-1*H*-tetrazole-5-thiol, prepared by reactions of organometallic azides with PhNCS, have been reported so far [1–6] and, based on infrared data, structures containing M–N(4) primary bonds between the metal and the heterocyclic ligand were proposed. Recently the first structural studies by X-ray diffraction on organotin derivatives were reported [7,8], pointing out that the primary bond of the tetrazolethiolato ligand occurs through sulfur, and not through nitrogen. Moreover, different coordination patterns of the ligand in the thiolic form have been found. In the monomeric $Bu_2Sn[SCN_4Ph]_2$ [7,8] the tetrazolethiolato ligand is monometallic biconnective (structure **a**, Sn–S 2.474(3), Sn · · · N(4) 2.975(5) Å [8]), while Bz_3SnSCN_4Ph exhibits a polymeric structure based upon bimetallic triconnective ligand units (structure **b**, av. Sn–S 2.589, Sn ← N(3) 2.617, Sn · · · N(4) 3.179 Å [8]).



a



b

We report now the crystal and molecular structure of the related trimethyltin derivative which exhibits an unusual trimeric structure, based upon intermolecular N → Sn coordinative bonds.

2. Results and discussion

1-Phenyl-1*H*-tetrazole-5-thiolato-trimethyltin(IV), Me_3SnSCN_4Ph, was prepared by reaction of Me_3SnCl with the ammonium salt of the heterocyclic ligand (see Experimental details). The NMR (^1H, ^{13}C, ^{119}Sn) data are consistent with a tetrahedral, monomeric structure in solution [7,8], while the magnitude of the Mössbauer

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quadrupole splitting (QS = 3.14 mm s^{-1}) suggests an increase of the tin coordination number in the solid state [7].

The solid structure was established by X-ray crystallography, the results of which are shown in Fig. 1. Important interatomic distances and angles are listed in Table 1.

Table 1
Selected interatomic distances (Å) and angles (deg) in the trimeric $[Me_3SnSCN_4Ph]_3$ unit

Intramolecular			
Sn(1)–S(1)	2.565(4)	C(1)–Sn(1)–C(2)	115.8(8)
Sn(1)–C(1)	2.130(21)	C(2)–Sn(1)–C(3)	120.3(1.0)
Sn(1)–C(2)	2.106(21)	C(1)–Sn(1)–C(3)	117.8(8)
Sn(1)–C(3)	2.101(19)	S(1)–Sn(1)–C(1)	93.1(5)
Sn(1) ··· N(4)	3.285(12)	S(1)–Sn(1)–C(2)	100.4(5)
		S(1)–Sn(1)–C(3)	100.9(5)
S(1)–C(4)	1.727(18)		
C(4)–N(1)	1.344(15)	Sn(1)–S(1)–C(4)	99.1(5)
N(1)–N(2)	1.351(25)	S(1)–C(4)–N(1)	127.3(1.4)
N(2)–N(3)	1.345(21)	S(1)–C(4)–N(4)	127.0(9)
N(3)–N(4)	1.295(19)		
N(4)–C(4)	1.321(26)		
Intermolecular			
Sn(1a) ← N(3b)	2.747(14)	S(1a)–Sn(1a) ← N(3b)	173.8(4)
		C(1a)–Sn(1a) ← N(3b)	81.9(7))
		C(2a)–Sn(1a) ← N(3b)	78.6(6)
		C(3a)–Sn(1a) ← N(3b)	84.8(6)

The primary bonding of the tetrazolethiolato ligand to tin occurs through its sulfur atom (Sn(1)–S(1) 2.565(4) Å, cf Σ_{COV}(Sn,S) = 2.42 Å [9]). The heterocyclic ring plane is oriented almost perpendicular (97.4°) to the Sn(1)C(2)C(3) plane, bringing the N(4) atom above this plane at 2.324 Å, thus allowing a weak intramolecular secondary interaction, Sn(1) ··· N(4) 3.285(12) Å. As a result the C(2)–Sn(1)–C(3) angle is larger than the other two C–Sn–C angles (120.3(10)° vs. 115.8(8)° and 117.8(8)°, respectively). The slight non-planarity of the SnC_3 moiety (Σ(C–Sn–C) = 353.9°) is consistent with the appearance of infrared absorptions assigned to SnC_3 stretching vibrations. Additionally, an intermolecular, dative Sn(1) ← N(3b) bond of 2.787(14) Å is established, thus increasing the coordination number of the central metal atom to 6. The resulting coordination polyhedron around the Sn(1) atom can be described as a capped trigonal bipyramid, with S(1) and N(3b) atoms in axial positions (S(1)–Sn(1)–N(3b) 173.8(4)°), carbon atoms of the

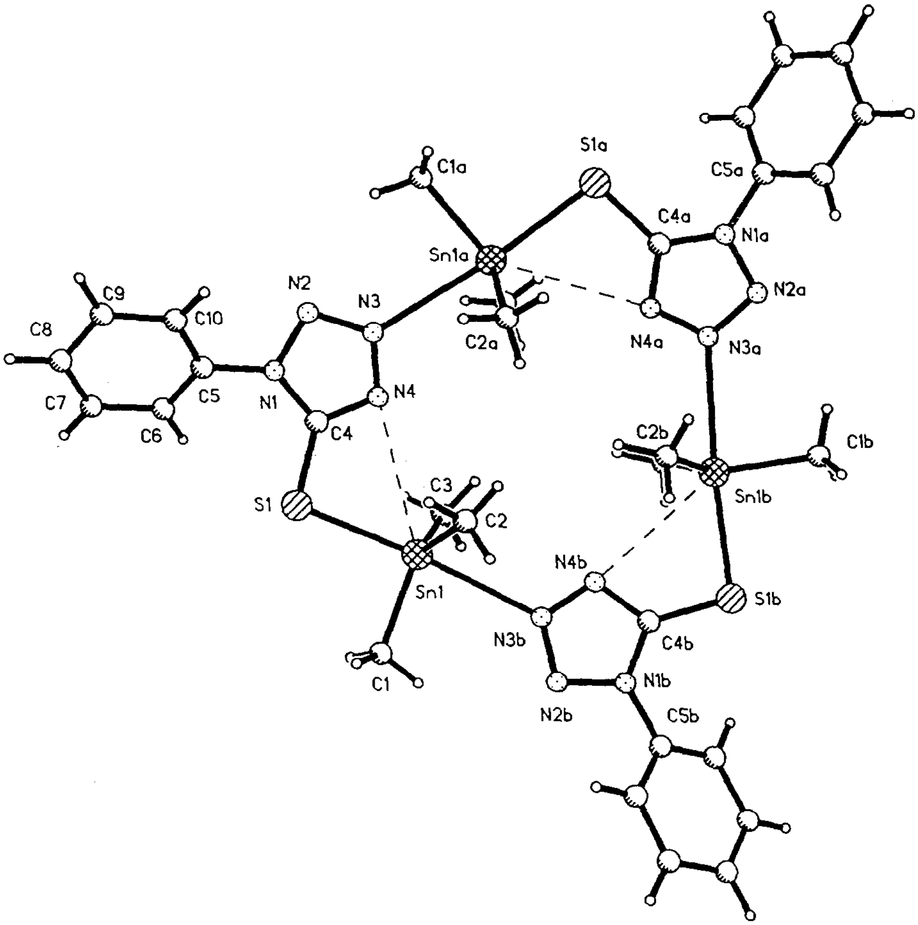

Fig. 1. View of the trimeric $[Me_3SnSCN_4Ph]_3$ unit, showing the atom numbering scheme.

Table 2
Tin–sulfur and tin–nitrogen distances

	R = Me	R = Bz [a] [8]
Sn–S, Å	2.565(4)	2.565(4), 2.614(5)
Sn · · · N(4) (*intra*), Å	3.285(12)	3.204(10), 3.156(10)
Sn ← N(3) (*inter*), Å	2.747(14)	2.676(10), 2.559(12)

[a] Two independent molecules are present in the unit cell.

methyl groups in equatorial ones, and the N(4) atom in the capping position.

As a consequence, in the title compound the tetrazolethiolato ligand can be regarded as a bimetallic triconnective bridge, as in the tribenzyltin(IV) analogue [8]. However, the association of the monomeric units of R_3SnSCN_4Ph in the crystal is completely different, i.e. chain polymeric for R = Bz, and, surprisingly, trimeric for R = Me (Fig. 1), with a fifteen-membered $Sn_3S_3C_3N_6$ ring. This behaviour is probably due to steric effects of the organic groups bonded to tin, the volume of the benzyl group being larger than that of the methyl one. A tetrameric structure of a trimethyltin(IV) phosphinate, $[Me_3SnO_2PPh_2]_4$ was also recently reported [10]. A comparison of the tin–sulfur and tin–nitrogen distances in the two tetrazolethiolato-triorganotin(IV) compounds, R_3SnSCN_4Ph, reveals other differences (Table 2).

Thus, while the Sn–S bond distances are of the same magnitude, both intra- and intermolecular tin–nitrogen distances are longer in the trimethyltin(IV) derivative than in the tribenzyltin(IV) analogue. This behaviour might be the result either of the difference in the electronic effects for the organic groups bonded to tin, or the association into trimer or polymer arrangement.

Further structural studies using different triorganotin moieties would be of interest, since, for example, although the Mössbauer data suggest a tetrahedral, monomeric structure in the solid state for the triphenyltin (IV) analogue, Ph_3SnSCN_4Ph [7], an X-ray diffraction investigation [11] has established a polymeric structure containing five-coordinated tin atoms, similar to that described previously for the tribenzyltin(IV) derivative [8].

3. Experimental details

3.1. Preparation of Me_3SnSCN_4Ph

NH_4SCN_4Ph (0.40 g, 2.06 mmol) was added to a solution of Me_3SnCl (0.41 g, 2.06 mmol) in CH_2Cl_2 (30 ml) and the reaction mixture was stirred for 7 h, under reflux. The resulting NH_4Cl was filtered off and the clear filtrate was concentrated in vacuum. A white crystalline solid was deposited and was filtered, washed with n-hexane, methanol and water, and dried in vacuo. Yield 0.4 g (59%), m.p. 142–3°. Elemental analysis, $C_{10}H_{14}N_4SSn$ requires C, 35.22; H, 4.13; N, 16.43. Found C, 35.01; H, 3.96; N, 16.33%. IR (KBr): 535m w, 505m ($\nu(SnC_3)$). NMR ($CDCl_3$): ^1H δ 0.73 (s, 9H, CH_3, $^2J(^{117,119}SnCH)$ 57.1, 59.2 Hz), 7.48 (m, 3H, *m*- and *p*-C_6H_5), 7.68 (d, 2H, *o*-C_6H_5); ^{13}C δ -1.96 (s, CH_3, $^1J(^{117,119}SnC)$ 366.7, 384.3 Hz), 124.07 (s, *o*-C_6H_5), 129.40 (s, *m*-C_6H_5), 129.57 (s, *p*-C_6H_5), 134.63 (s, *i*-C_6H_5), 156.23 (s, *C*–S); ^{119}Sn δ 106.95 [8]. Mössbauer: IS 1.36, QS 3.14 [7]. Suitable crystals for X-ray diffractometry were obtained from CH_2Cl_2/n-hexane, by solvent diffusion over a period of 10 days at room temperature.

3.2. Crystal structure determination of Me_3SnSCN_4Ph

Crystal data: $C_{10}H_{14}N_4SSn$, M = 341.0, rhombohedral, space group *R*3, $a = 18.097(4)$, $c = 10.832(5)$ Å, $V = 3073(2)$ Å^3, $Z = 9$, $D_c = 1.658$ g cm^{-1}, $\lambda = 0.71073$ Å, $\mu = 2.005$ mm^{-1}, $F(000) = 1512$, T = 293 K.

Data were collected on a Siemens P4 diffractometer for $3.0 < 2\theta < 45.0°$. The structure was solved by direct methods and full-matrix least-squares refinement (145 parameters) converged to final residual indices $R = 3.49\%$, $wR = 4.03\%$, S = 1.23 using 663 data for which $I > 3.0\sigma(I)$. Hydrogen atoms were calculated as a riding model with fixed isotropic U. $R = \Sigma|\Delta|/\Sigma|F_o|$; $wR = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$; $S = [\Sigma w\Delta^2/(N.O. - N.V.)]^{1/2}$; $\Delta = F_o - F_c$.

Details on the data collection, solution and refinement, the atomic coordinates, thermal parameters, and a complete list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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