Crystal structure
of triphenyl(5-mercapto-1-phenyl-1,2,3,4-tetrazolato)tin(IV)

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Abstract

The title compound was prepared from 1-phenyl-5-thione-1,2,3,4-tetrazole and triphenyltin(IV) hydroxide and its crystal structure was determined by X-ray diffraction. The lattice is formed by discrete molecules that contain the tin atom coordinated to three phenyl groups and to the tetrazole via the deprotonated –SH group in a distorted tetrahedral coordination polyhedron. There is evidence of a very weak intramolecular interaction between N(4) of the tetrazole and the Sn atom. ^{13}C and ^{15}N NMR studies (CDCl$_3$) suggest that in solution the tetrazole is also in the deprotonated thiol form, and binds to the tin via its S atom.

Key words: Tin; X-ray structure; Tetrazole

1. Introduction

Cycloaddition of azide ion to organic isothiocyanates gives 1-substituted-5-thione tetrazoles [1]. Triorganotin azides also undergo this reaction to give metallated 1-substituted tetrazoles [2]. Initially for phenyl isothiocyanate metallation at N(4) was assumed [2], in accordance with reaction (1)

$$\text{PhNCS} + \text{SnR}_3\text{N}_3 \longrightarrow \text{[structure]} \quad (1)$$
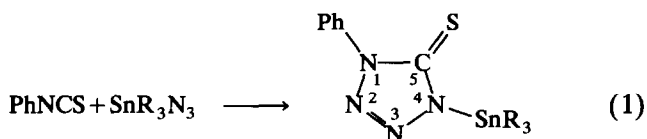
Subsequently, the crystal structure of dibutylbis(5-mercapto-1-phenyl-1,2,3,4-tetrazolato)tin(IV) (prepared by a different method [3]) showed that in this

complex each tetrazole is bound via the deprotonated thiol group, suggesting similar S–Sn coordination for the triorganotin(IV) derivatives of this type of heterocycle.

Triphenyl(5-mercapto-1-phenyl-1,2,3,4-tetrazolato)tin(IV) can be prepared from triphenyltin azide and phenyl isothiocyanate via reaction (1) [2], or by reaction of the preformed tetrazole and a suitable tin(IV) derivative [3]. In this work we synthesized this product by a novel variant of the latter method, determined its crystal structure and recorded its ^{13}C and ^{15}N NMR spectra, all of which confirmed coordination via the sulphur atom.

2. Experimental section

2.1. Reagents

1-Phenyl-5-thione-1,2,3,4-tetrazole (HL) (Ega Chemie) and triphenyltin(IV) hydroxide (Aldrich) were used as supplied.

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2.2. Synthesis of triphenyl(5-mercapto-1-phenyl-1,2,3,4-tetrazolato)tin(IV), [SnPh₃(L)]

The compound was prepared by a novel synthetic route involving direct reaction of the preformed HL and triphenyltin(IV) hydroxide. HL (0.8 g, 4.5 mmol) and SnPh₃OH (1.65 g, 4.5 mmol) in methanol (50 ml) were stirred under reflux for 48 h, after which the reaction mixture was concentrated *in vacuo* to give a colourless crystalline solid which was filtered off and dried under vacuum. M.p. 137°C (lit. 129–137 [2] and 139–140°C [3]). Anal. calcd. for $C_{25}H_{20}N_4SSn$, C 56.9, H 3.8, N 10.6; found, C 57.2, H 3.8, N 10.5%.

2.3. Physicochemical measurements

^{13}C and ^{15}N NMR spectra were recorded in saturated $CDCl_3$ solutions on a Bruker AMX-500 spectrometer. Shifts in ppm were referred to TMS using the solvent and pure nitromethane signals, respectively. Other physicochemical measurements were as described previously [4].

2.4. Crystal structure determination

Crystal data: $C_{25}H_{20}N_4SSn$; M = 527.22; monoclinic, space group $P2_1/n$, $a = 10.999(1)$, $b = 16.218(2)$, $c = 13.185(1)$ Å, $\beta = 100.58(1)°$, $U = 2311.9(7)$ Å³ (by least-squares refinement of the setting angles for 25 automatically centred reflections, $10 < \theta < 20°$, $\lambda = 0.71073$ Å), $Z = 4$, $D_c = 1.52$ g cm⁻³. The irregularly shaped crystal had maximum and minimum linear dimensions of 0.45 and 0.02 mm, μ(Mo Kα) = 12.13 mm⁻¹.

Data Collection and Processing: CAD4 diffractometer, $\omega/2\theta$ mode with scan width $\omega = 0.8 + 0.55$ tan θ; graphite monochromated Mo Kα radiation, 3982 reflections measured ($0 < \theta < 25°$, $-13 \le h \le 12, 0 \le k \le 19, 0 \le l \le 15$), 3817 unique (merging $R = 0.042$), and 3200 with $I > 3\sigma(I)$; Lorentz and polarization corrections were applied and, at a later stage in the refinement, absorption corrections [5] (max., min. correction factors 1.30, 0.80 respectively). The intensity of two standard reflections remained essentially constant throughout the experiment.

Structure Analysis and Refinement: The structure was solved by the standard heavy-atom Patterson method followed by normal difference Fourier techniques and blocked matrix least-squares refinement with all non-H atoms anisotropic. H atoms were included as fixed contributors at positions calculated on stereochemical grounds, and with an overall isotropic temperature factor that refined to 0.089(3) Å². The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weighting scheme $w = 1/[\sigma^2(F_o) + 0.0002*F_o^2]$, which gave final R [$= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$] and R' {$= [w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$} of 0.0285 and 0.0304,

TABLE 1. Fractional atomic coordinates and equivalent isotropic temperature factors (Å²)

|	x	y	z	B_{iso}
Sn	0.0446(1)	0.2616(1)	0.6411(1)	3.206(8)
S	0.0777(1)	0.3555(1)	0.7923(1)	4.08(3)
N(1)	0.2997(2)	0.3789(2)	0.9187(2)	3.28(9)
N(2)	0.4209(3)	0.3569(2)	0.9265(2)	4.2(1)
N(3)	0.4256(3)	0.3108(2)	0.8478(2)	4.2(1)
N(4)	0.3123(3)	0.3018(2)	0.7873(2)	3.9(1)
C(5)	0.2353(3)	0.3438(2)	0.8328(3)	3.3(1)
C(11)	0.2612(3)	0.4335(2)	0.9915(3)	3.3(1)
C(12)	0.3198(3)	0.5087(2)	1.0093(3)	4.0(1)
C(13)	0.2844(4)	0.5612(3)	1.0812(3)	5.1(1)
C(14)	0.1908(4)	0.5389(3)	1.1318(3)	5.8(2)
C(15)	0.1310(4)	0.4642(3)	1.1121(3)	5.7(2)
C(16)	0.1676(3)	0.4092(3)	1.0416(3)	4.4(1)
C(111)	-0.1498(3)	0.2816(2)	0.6152(3)	3.3(1)
C(112)	-0.2167(3)	0.3139(2)	0.5239(3)	4.2(1)
C(113)	-0.3408(4)	0.3329(3)	0.5159(3)	5.4(2)
C(114)	-0.3977(3)	0.3206(3)	0.5981(4)	6.0(2)
C(115)	-0.3352(4)	0.2878(3)	0.6884(3)	5.3(2)
C(116)	-0.2112(3)	0.2691(2)	0.6971(3)	4.2(1)
C(121)	0.0989(3)	0.1440(2)	0.7037(3)	3.5(1)
C(122)	0.2214(3)	0.1199(2)	0.7334(3)	4.5(1)
C(123)	0.2503(4)	0.0453(3)	0.7828(3)	5.3(2)
C(124)	0.1589(4)	-0.0063(3)	0.8034(3)	5.3(2)
C(125)	0.0373(4)	0.0153(2)	0.7716(3)	4.9(1)
C(126)	0.0069(3)	0.0897(2)	0.7223(3)	4.0(1)
C(131)	0.1343(3)	0.3210(2)	0.5319(3)	3.8(1)
C(132)	0.0832(4)	0.3940(3)	0.4867(3)	5.3(2)
C(133)	0.1420(6)	0.4364(3)	0.4187(4)	7.6(2)
C(134)	0.2507(6)	0.4081(4)	0.3961(4)	7.8(2)
C(135)	0.3009(4)	0.3378(4)	0.4393(4)	6.9(2)
C(136)	0.2418(4)	0.2925(3)	0.5070(3)	5.1(1)

$B_{iso} = 4/3\Sigma_{ij}B_{ij}a_i a_j.$

respectively. A final difference Fourier map showed no features of chemical significance. Programs used were SHELX76 [6] and ORTEP [7]. Scattering factors for non-H atoms were from Cromer and Mann [8], with corrections for anomalous dispersion from Cromer and Liberman [9] and, for H atoms, from Steward, Davidson and Simpson [10]. The final atomic coordinates are listed in Table 1. Full tables of parameters have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. ^{13}C and ^{15}N NMR studies in $CDCl_3$ solution

The structural changes occurring in HL upon deprotonation and coordination to the Sn atom should be reflected by the changes in the C(5) signal of its ^{13}C NMR spectrum. If the initial thione form of HL changes to the thiolate upon complexation (reaction 2),

$$Ph \diagdown N - C \diagup S \qquad + \ SnPh_3OH \ \longrightarrow$$

$$Ph \diagdown N - C \diagup S - SnPh_3 \qquad + \ H_2O \qquad (2)$$
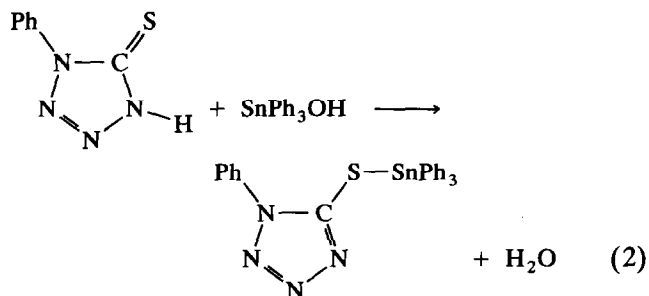
C(5) should be further upfield in the spectrum of [SnPh$_3$(L)] than in that of HL, the shielding effect of the C=N bond being greater than that of the C=S bond [11]. This is the case, the C(5) signal shifting upfield from 163.5 ppm in HL to 153.6 ppm in the complex.

In the ^{15}N NMR spectrum of HL there were four signals at -145.6, -144.2, -28.9 and -23.0 ppm, consistent with the data for 1-methyl-5-thio-1,2,3,4-tetrazole (HL') [12] (if the signs of the shifts for HL' are reversed). These signals were assigned to N(1), N(4), N(2), and N(3), respectively. Upon complexation, all the nitrogen atoms are deshielded and the four signals are shifted to -143.6 [N(1)], -54.6 [N(4)], -12.1 [N(2)], and 5.2 [N(3)] ppm. It should be noted that N(4) experiences the greatest shielding, which also occurs in the S-methylated (MeL') [12]. This clearly supports the suggested thione-to-thiol tautomerization prior to formation of the S–Sn bond in [SnPh$_3$(L)].

3.2. Crystal structure

Figure 1 shows the structure and atomic numbering scheme of [SnPh$_3$(L)]. The interatomic distances and angles around the tin atom are listed in Table 2 and Table 3 lists those in the ligand moiety.

The compound is formed by discrete molecules in which the tin atom is indeed bound to the sulphur
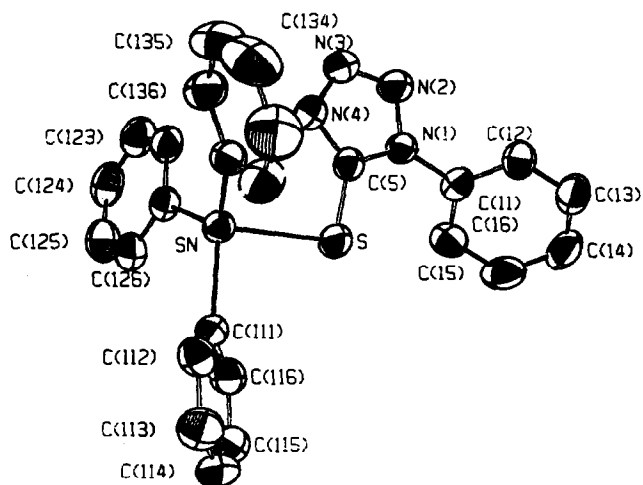

Fig. 1. Perspective view of (SnPh$_3$(L)) showing the atom numbering scheme.

atom of the tetrazolate, which together with the phenyl groups defines a distorted tetrahedron around the metal. There is also an intramolecular tin–nitrogen N(4) short contact of 3.275(3) Å, shorter than the sum of the van der Waals' radii (3.75 Å) [13]. The S–Sn–C bond angles are more acute and the C–Sn–C bond angles larger than the theoretical tetrahedral angle, the

TABLE 2. Interatomic distances (Å) and angles (°) around the Sn atom with e.s.d.'s in parentheses

Sn–S	2.482(1)
Sn–C(111)	2.127(3)
Sn–C(121)	2.120(3)
Sn–C(131)	2.120(4)
S–Sn–C(111)	91.73(9)
S–Sn–C(121)	104.48(9)
S–Sn–C(131)	104.4(1)
C(111)–Sn–C(121)	113.7(1)
C(111)–Sn–C(131)	113.6(1)
C(121)–Sn–C(131)	122.7(1)

TABLE 3. Interatomic distances (Å) and angles (°) in the ligands with e.s.d.'s in parentheses

S–C(5)	1.728(4)	N(1)–N(2)	1.365(4)
N(1)–C(5)	1.347(5)	N(1)–C(11)	1.426(5)
N(2)–N(3)	1.288(4)	N(3)–N(4)	1.358(4)
N(4)–C(5)	1.314(5)	C(11)–C(12)	1.379(5)
C(11)–C(16)	1.379(5)	C(12)–C(13)	1.382(6)
C(13)–C(14)	1.374(6)	C(14)–C(15)	1.380(7)
C(15)–C(16)	1.400(6)	C(111)–C(112)	1.393(5)
C(111)–C(116)	1.390(5)	C(112)–C(113)	1.384(6)
C(113)–C(114)	1.362(6)	C(114)–C(115)	1.368(7)
C(115)–C(116)	1.381(6)	C(121)–C(122)	1.388(5)
C(121)–C(126)	1.397(5)	C(122)–C(123)	1.383(6)
C(123)–C(124)	1.373(6)	C(124)–C(125)	1.372(7)
C(125)–C(126)	1.382(5)	C(131)–C(132)	1.396(6)
C(131)–C(136)	1.365(5)	C(132)–C(133)	1.381(7)
C(133)–C(134)	1.364(9)	C(134)–C(135)	1.347(9)
C(135)–C(136)	1.404(7)		
Sn–S–C(5)	99.9(1)		
N(2)–N(1)–C(5)	108.0(3)		
N(2)–N(1)–C(11)	121.2(3)		
C(5)–N(1)–C(11)	130.8(3)		
N(1)–N(2)–N(3)	105.9(3)		
N(2)–N(3)–N(4)	111.5(3)		
N(3)–N(4)–C(5)	105.9(3)		
S–C(5)–N(1)	123.8(3)		
S–C(5)–N(4)	127.6(3)		
N(1)–C(5)–N(4)	108.6(3)		
N(1)–C(11)–C(12)	118.4(3)		
N(1)–C(11)–C(16)	119.0(3)		
Sn–C(111)–C(112)	123.5(3)		
Sn–C(111)–C(116)	118.1(2)		
Sn–C(121)–C(122)	123.5(3)		
Sn–C(121)–C(126)	118.3(2)		
Sn–C(131)–C(132)	118.3(3)		
Sn–C(131)–C(136)	122.8(3)		

largest deviations occurring in S-Sn-C(111) [91.73(9)°] and C(121)-Sn-C(131) [122.7(1)°] (see Table 2). This is possibly due to the secondary interaction between Sn and N(4). The Sn-S distance [2.482(1) Å] is greater than the sum of the covalent radii (2.42 Å [14]) (as occurs in [SnBu$_2$(L)$_2$] [3]) and greater than the tin–sulphur distances in triphenyltin thioaryloxides [15], mono- and dithiocarbamates [16], xanthates [17], dithiophosphates [18], and thiosemicarbazonates [19]. In fact, in neutral complexes containing triphenyltin, such a long distance has only been observed in [SnPh$_3$(S$_2$CN(CH$_2$)$_5$)] (2.481(2) Å) [20] and in one of the four independent molecules of 5-amino-1,3,4-thiadiazolyl-2-thiolatotriphenyltin (2.481(2) Å) [21]. However, in [SnPh$_3$(S$_2$C$_2$(CN)$_2$)]$^-$, the shorter of the two Sn-S distances is 2.496(2) Å [22].

In the tetrazolate, the C(5)-S bond length [1.728(4) Å] lies between the average value for the double C=S bond in thioureas (1.681 Å [23]) and the single C-S bond in the C-S-Me fragment (1.789 Å [23]), suggesting that the carbon–sulphur bond has some double-bond character in the deprotonated tetrazole. The C-S bond in [SnBu$_2$(L)$_2$] [1.76(2) Å] [3] does not show this effect to such a degree. However, in both those complexes the observed sequence of bond lengths in the five-membered ring is the same and suggests bond multiplicities as shown in the canonical form of the thiolate in reaction 2. That is, short C(5)-N(4) and N(2)-N(3) bonds and long N(1)-C(5), N(1)-N(2) and N(3)-N(4) bonds (see Table 2). The ring is essentially planar and forms a dihedral angle of 54.7(4)° with the planar 1-phenyl ring. The bond angles within the phenyl rings are all close to 120°.

Acknowledgment

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