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Note

An exact coordination mode of 6-thiopurine with an organotin(IV): preparation and crystal structure of triphenyl(6-thiopurinyl)tin(IV)

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Abstract

Triphenyl(6-thiopurinyl)tin has been prepared and its structure reinvestigated by X-ray diffraction. In the structure, a new coordination mode was observed that was different from those reported previously from investigations by infrared and Mössbauer spectroscopy. In the molecule, 6-thiopurine coordinated to tin by the S and N(1) atoms. The discrete molecules were connected to form a zigzag 1D network through intermolecular H···N hydrogen bonds. The tin environment is pentacoordinated with *cis*-trigonal bipyramidal geometry.

Keywords: Crystal structure; Coordination mode; Donor atom; 6-Thiopurine

1. Introduction

6-Thiopurine (6-TPH) is an anticancer antimetabolite (inter alia), clinically effective against human leukemias [1], so its complexes with organotin(IV) derivatives also exhibiting anticancer activity have been studied [2–4]. It has been observed that 6-TPH showed tautomerism between the thiol and thione isomers. Depending on the different alkyl groups in organotin compounds, 6-TP$^-$ coordinated to tin by different donor atoms and presented different coordination modes. For instance, in Me_3Sn(6-TP), 6-TPH adopted the thione form and coordinated to tin by the N(1) and N(2) atoms, attaining a polymeric trigonal bipyramidal structure, as shown in Fig. 1(a). As far as $^nBu_2Sn$(6-TP)$_2$ is concerned, it adopted the thiol form and the primary Sn–S bond was stabilized through chelation of tin by the N(3) atom of the purine ring, as shown in Fig. 1(b).

With three bulky phenyl groups, Ph_3Sn(IV) is much represented in studies about the effect of alkyl groups on the selection of coordination modes and donor atoms. According to the data of infrared and Mössbauer spectroscopy, Barbieri et al. [3,4] concluded that the product of the reaction of Ph_3Sn(IV) derivatives with 6-TPH was a unique complex. Its possible structure was assumed to be a linear polymer, in which 6-TP$^-$ is coordinated to the tin atom by S, N(2) and N(4) atoms, as shown in Fig. 1(c). Based on the interest in the metabolic coordination behavior of 6-TPH, we prepared Ph_3Sn(6-TP) and reinvestigated its crystal structure by X-diffraction. This work is performed to ascertain the coordination mode that would be adopted and which nitrogen atoms of the purine ring would be attacked by Ph_3Sn^+. The result did not agree with Barbieri's previous conclusion [2,3].

2. Results and discussion

2.1. Synthesis aspects of $C_{23}H_{18}N_4SSn$

It has been reported that the reactions of Ph_3SnOH with 6-TPH (1:1) in hot acetone [2] and hexaphenyldistannoxane with 6-TPH in boiling acetone afforded a

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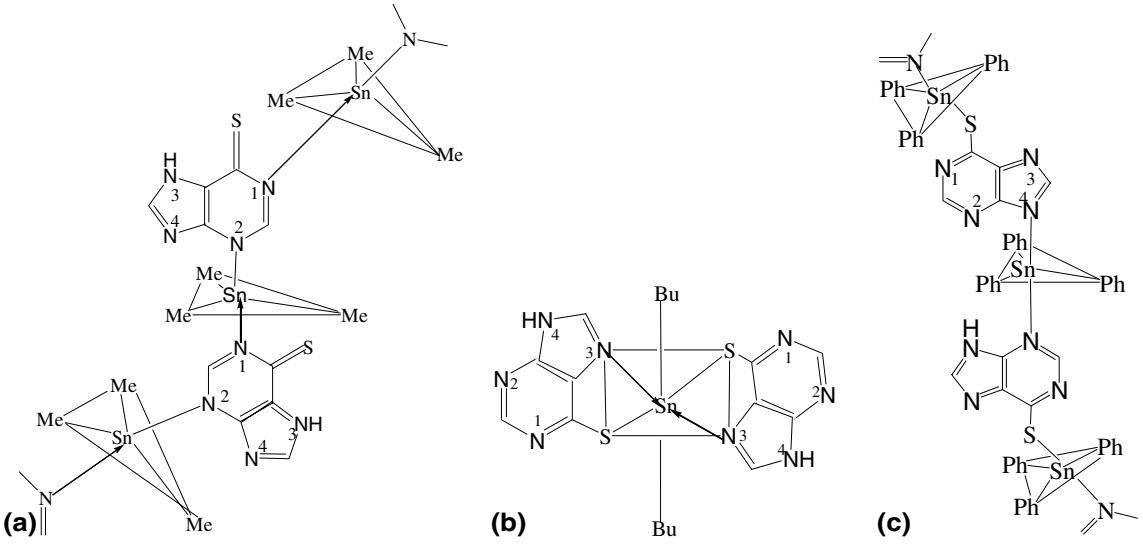

Fig. 1. The possible coordination modes for $Me_3Sn(6\text{-TP})$, $^nBu_2Sn(6\text{-TP})_2$ and $Ph_3Sn(6\text{-TP})$.

product with the unexpected stoichiometry $Ph_3Sn(IV)$: 6-TPH = 3:2 [5]. Instead, another synthetic route was taken: reaction of Ph_3SnCl with 6-TPH(1:1) in hot methanol, the product being obtained by deprotonation of 6-TPH with methoxide. In this reaction, 6-TP^- was electrophilically attacked by Ph_3Sn^+. Mono-deprotonation of 6-TPH would take place at N(1) [6,7], with the negative charge residing on the sulfur atom of the resulting 'aromatic' tautomer [6]. As a consequence, it could be expected that S-stannylation of 6-TPH primarily occurs, where one 6-TP^- is bound to $Ph_3Sn(IV)$.

2.2. Description of the crystal structure of $C_{23}H_{18}N_4SSn$

Further structural information was obtained by X-ray diffraction characterization of the solid (Table 1). In the unit cell of this compound, there are two crystallographically independent molecules that show only minor differences. A molecular view is shown in Fig. 2 and the unit cell is shown in Fig. 3.

From the X-ray diffraction data (Table 2), there exist two monomers in the asymmetric unit which are different from a crystallographic point of view. Conformations of the two independent molecules are almost the same, with only little differences in bond lengths and bond angles. For molecular A, it may be seen that the bond length of Sn(1)–S(1) (2.442(4) Å) lies toward the middle of the range reported for triphenyltin heteroarenethiolates (2.405–2.481 Å) and approaches the sum of the covalent radii of tin and sulfur (2.42 Å) [8,9], which proves that the sulfur atom is coordinated to the tin atom by a strong chemical bond. Besides the Sn–S primary bond, there is also an intramolecular Sn–N interaction, common in thiolate ligands having nitrogen donor atoms [10–16]. The bond distance of Sn(1)–N(1) (2.95(5) Å) is midway between the sums of the van der Waals and covalent radii of tin and nitrogen (2.15–3.74 Å) [17], and the interaction can be regarded as a weak coordinate bond. The bond C(4)–S(1) (1.726 Å) is consistent with the C–S single bonds (1.724 and 1.730 Å) in products of the reaction of triphenyltin with 1-methyltetrazole-5-thiolate and benzoxazole-2-thiolate ligands, respectively [18], and this shows that C–S exists as single bond and is indirect evidence that the ligand is coordinated to tin as the thiol but not as the thione isomer. The coordination mode is in accordance with the nature of the Sn–S chemical bond.

Table 1
Crystal data and measurement conditions for $C_{23}H_{18}N_4SSn$

Empirical formula	$C_{23}H_{18}N_4SSn$
Formula weight	501.16
T (K)	298(2)
Crystal system	orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	15.437(3)
b (Å)	19.135(4)
c (Å)	36.213(6)
V (Å^3)	10697(3)
Z	16
Absorption coefficient, μ (mm^{-1})	1.046
θ Range for data collection (°)	1.12–24.84
Number of reflections collected	50985
Number of independent reflections (R_{int})	8913
Goodness-of-fit (on F^2)	0.817
Final R indices [$I > 2.0\sigma(I)$]	$R_1 = 0.0622$, $wR_2 = 0.1426$
R indices (all data)	$R_1 = 0.2233$, $wR_2 = 0.2203$
Largest difference peak and hole (e Å^{-3})	0.086 and −0.517

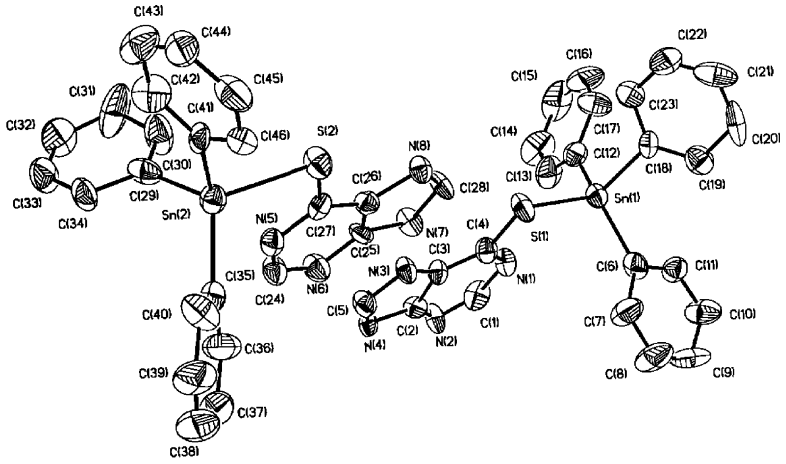

Fig. 2. An ORTEP representation of the molecular structure of the title compound.

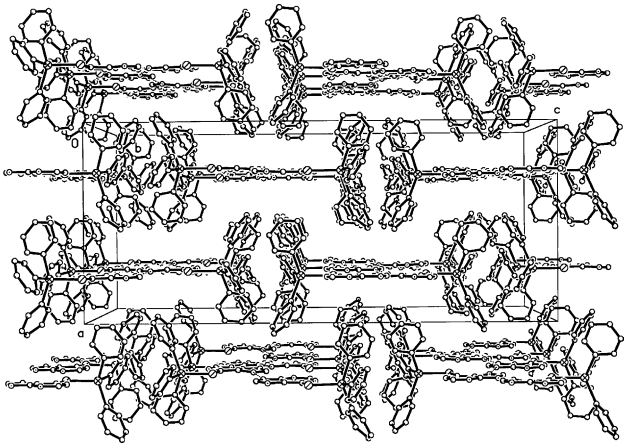

Fig. 3. Unit cell of the title compound.

Described as above, besides the primary S atom, the N atom attacked by Ph_3Sn^+ was N(1) but not N(2) atom, which is not in agreement with Barbieri's previous conclusion [2,3]. According to the infrared and Mössbauer spectroscopic data reported previously, it has been predicted that the sites of primary attack of 6-TP by $R_nSn(IV)$ moieties are the S and N(2) atoms, and Fig. 1(c) shows the possible structure of $Ph_3Sn(6\text{-TP})$ [3]. But now, the X-ray diffraction data testify that 6-TP^- is attacked by Ph_3Sn^+ at S and N(1) sites and the structure of $Ph_3Sn(6\text{-TP})$ is as shown in Fig. 3. The results exhibit a new coordination mode for 6-TPH, which proves that, besides N(2), N(3) and N(4) atoms [2,3], the N(1) atom also has coordination ability.

As shown in Fig. 3, there are also intermolecular hydrogen bonds (N···H) between N and H atoms, such

Table 2
Selected bond lengths (Å) and angles (°) for $C_{23}H_{18}N_4SSn$

Molecule A		Molecule B	
Sn(1)–C(6)	2.063(15)	Sn(2)–C(35)	2.125(13)
Sn(1)–C(12)	2.108(15)	Sn(2)–C(29)	2.126(14)
Sn(1)–C(18)	2.138(15)	Sn(2)–C(41)	2.132(14)
Sn(1)–S(1)	2.442(4)	Sn(2)–S(2)	2.444(4)
Sn(1)–N(1)	2.958(11)	Sn(2)–N(5)	2.978(11)
C(4)–S(1)	1.726(14)	C(4)–S(1)	1.748(14)
N(4)–H(4)	0.860	N(7)–H(7)	0.860
N(3)–H(7)	1.913	N(8)–H(4)	1.910
C(6)–Sn(1)–C(12)	116.5(5)	C(35)–Sn(2)–C(29)	118.0(5)
C(12)–Sn(1)–S(1)	113.2(4)	C(35)–Sn(2)–C(41)	108.4(5)
C(6)–Sn(1)–S(1)	110.9(4)	C(29)–Sn(2)–C(41)	106.4(5)
C(6)–Sn(1)–C(18)	108.4(5)	C(35)–Sn(2)–S(2)	112.3(3)
C(12)–Sn(1)–C(18)	107.0(5)	C(29)–Sn(2)–S(2)	111.2(4)
C(18)–Sn(1)–S(1)	99.2(3)	C(41)–Sn(2)–S(2)	98.6(3)
N(1)–Sn(1)–C(6)	81.0(4)	N(5)–Sn(2)–C(29)	80.4(4)
N(1)–Sn(1)–C(12)	85.5(5)	N(5)–Sn(2)–C(35)	86.8(4)
N(1)–Sn(1)–C(18)	157.4(4)	N(5)–Sn(2)–C(41)	156.6(4)
N(1)–Sn(1)–S(1)	58.3(2)	N(5)–Sn(2)–S(2)	58.5(2)
N(4)–H(4)–N(8)	158.63	N(7)–H(7)–N(3)	158.28

as H(4) and N(8) (1.910 Å), and H(7) and N(3) (1.913 Å), which associate discrete molecules into a zigzag 1D network.

Around the tin atom, the angles C(6)–Sn–C(12) (116.5(5)°), C(12)–Sn–S(1) (113.2(4)°) and C(6)–Sn–S(1) (110.9)(4)°) are wider while C(6)–Sn–C(18) (108.4(5)°) and C(12)–Sn–C(18) (107.0(5)°) are narrower than the ideal tetrahedral angle. Considering the Sn···N weak coordination, the structural distortion for the tin atom is best described as a displacement from tetragonal towards trigonal bipyramidal geometry.

3. Experimental

3.1. Preparation of $C_{23}H_{18}N_4SSn$

The reaction was carried out under nitrogen atmosphere with use of standard Schlenk technique. 6-TPH (0.17 g, 1 mmol) was added to the solution of methanol (20 ml) with sodium methoxide (0.054 g, 1 mmol), and the mixture was stirred for 30 min, after which Ph_3SnCl (0.385 g, 1 mmol) was added, the reaction continuing for 12 h at 60 °C. After cooling to room temperature, the mixture was filtered and the solvent was gradually removed from filtrate by evaporation under a vacuum until a solid product was obtained. This was then recrystallized from methanol to form colorless crystals of the complex. Yield, 72%. M.p. 218–220 °C The C, H, N and S analyses were performed using a Perkin–Elmer PE-2400II CHNS Micro-analyser. Found: C, 55.10; H, 3.63; N, 11.21; S, 6.41%. *Anal.* Calc. for $C_{23}H_{18}N_4SSn$: C, 55.12; H, 3.62; N, 11.18; S, 6.40. IR(KBr, cm^{-1}): 3330 (s, N–H), 535 (m, Sn–C), 307 (m, Sn–S).

3.2. X-ray structure analysis for $C_{23}H_{18}N_4SSn$

A crystal was mounted in a Lindemann capillary under nitrogen. Diffraction data were collected using a Siemens CCD area-detector and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A semiempirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 [19] and refined against F^2 by full-matrix least-squares using SHELXL-97 [20]. Hydrogen atoms were placed in calculated positions.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-192934. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambrige, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www http://www.ccdc.cam.ac.ck).

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