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Synthesis and crystal structure of [1,2-benzenedithiolate-(2–)-*S*,*S*′]bis{methyl-1,3-dithia-benzo[*c*]-2-stannolanyl}, [$(CH_3Sn)_2(C_6H_4S_2)_3$]

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Abstract

The reaction of sodium 1,2-benzenedithiolate with methyltin trichloride in water gives the benzenedithiolate of methyltin(IV) as a yellow precipitate. The structure of this compound has been determined by single-crystal X-ray diffractometry. The molecule consists of two benzo[*c*]1,2,3-dithia-stannolanyl moieties held together by a bridging benzene-1,2-dithiolate ligand. The geometry about the tin could be described as distorted tetrahedral, even if in view of the short intramolecular Sn · · · S contacts the structure is better regarded as involving pentacoordinate tin in a distorted trigonal bypyramid.

Introduction

The preparation and structural characterization of organotin thiolates have recently attracted attention. A variety of techniques have been employed, and particularly IR and NMR spectroscopy [1–7]. Cyclic dialkyltin dithiolates have been the most extensively studied, and in the case of 2,2-dimethyl- [8,9], 2,2-di-n-butyl- [10] and 2,2-di-t-butyl-1,3,2-dithiastannolanes [11] the crystal structures have been determined. These compounds are monomeric in solution, but intermolecular S · · · Sn interactions can give rise to association in solid depending on the nature of the alkyl group; thus the interaction is strong in the dimethyltin, weak in the di-n-butyl, and absent in the di-t-butyl derivative.

Dithiaorganostannolanes with only one alkyl group bonded to the tin have received a little attention in the cased of acyclic thiolates of the type $RSn(SR')_3$. The methyltin ethane-1,2-dithiolate, $(CH_3Sn)_2(C_2H_4S_2)_3$ was reported previously [3], and we recently reported the synthesis of 2-chloro-2-n-butyl-1,3-dithia-2-stannolane and crystal structure of its 1,10-phenanthroline complex [12]. We describe below the preparation and the crystal structure of [1,2-benzenedithiolate(2–)-*S*,*S*′]-bis{2-methyl-1,3-dithiabenzo[*c*]-2-stannolanyl}.

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Experimental

Commercial methyltin trichloride and benzene-1,2-dithiol were used as supplied. The title compound separated as a yellow microcrystalline solid when a solution of benzene-1,2-dithiol (1.0 g, 7.0 mmol) and sodium hydroxide (0.56 g, 14.0 mmol) in nitrogen-purged water was added to a solution of methyltin trichloride (1.1 g, 4.6 mmol) in water (10 ml). The same product was obtained when methyltin trichloride and benzenedithiol were used in a 1/1 molar ratio. Suitable crystals for the X-ray study (m.p. 186 °C) were obtained by recrystallization from a dichloromethane/n-hexane mixture.

The IR (KBr pellet) and far-IR spectrum (Nujol mull, polyethylene optics) recorded on a Nicolet 5SXC and a FAR 20F vacuum spectrometer, showed the following relevant bands: 527 cm^{-1}, attributable to the Sn–C stretching, and 382, 373, 357, 335 cm^{-1} in the Sn–S stretching region typical for organotin thiolates [1,13].

A signal at +94.1 ppm (relative to tetramethyltin) was found in the ^{119}Sn NMR spectrum obtained with a JEOL FX 90Q spectrometer at 22.5 °C in deuterochloroform solution. (A shift of +101.5 ppm was previously reported for the acyclic analogue $CH_3Sn(SPh)_3$ as a neat liquid [14].)

Crystallography.

The crystals examined, while large, were of poor habit, being split or broken tubes or fragments. Details of crystal data, measurement of intensities and data processing are summarized in Table 1. An empirical absorption correction, based on measurements of eight reflections at $X \approx 90°$ for different azimuthal angles (ψ-scan), was made and the transmission factor ranged from 0.005 to 0.021. Reversal of the direction of the polar axis gave a significantly larger R factor (0.045, compared with 0.039 for the structure reported). Fractional atomic coordinates and thermal parameters are given in Table 2, and selected bond lengths and angles in Table 3. Other geometrical details (planes of best fit for the ligands, deviations of atoms from the planes, dihedral angles between them and selected torsion angles) are reported in Table 4. Additional data, including hydrogen atom coordinates, anisotropic temperature factors, a complete list of bond distances and angles and a listing of observed and calculated structure factors are available from the authors.

Discussion

The structure of [1,2-benzenedithiolate(2–)-*S*,*S*′]-bis{2-methyl-1,3-dithiabenzo-[*c*]-2-stannolanyl} is shown in Fig. 1 (ORTEP) [15] and from another viewpoint in Fig. 2. The structure consists of discrete molecules, in which two 1,3-dithia-2-stannaindenyl moieties are connected via a bridging benzene-1,2-dithiolate ligand. Each of the two Sn^{IV} atoms is bonded to two sulphur atoms within the five-membered ring and one sulphur and a carbon atom out of the ring. The Sn–C, Sn–S and S–C bond lengths (cf. Table 3) are fairly close to the sum of the relevant covalent radii [16], and are in the range of the corresponding distances in organotin thiolates [9–12,17]. The geometry around each tin is almost identical, and could be described as a distorted tetrahedral, with angles ranging from 91.5(1) to 122.7(1)° for Sn(1) and from 90.0(1) to 120.9(1)° for Sn(2). In particular, there are large deviations

Table 1

Structure determination summary

Crystal data	
Empirical formula	$C_{20}H_{18}S_6Sn_2$
Color; habit	Yellow; prismatic
Crystal size (mm)	$0.3 \times 0.6 \times 0.9$
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	$a = 23.213(2)$ Å $b = 9.660(1)$ Å $c = 10.860(2)$ Å
Volume	2435.3(6) Å^3
Z	4
Formula weight	688.1
Density (calc.)	1.877 Mg/m^3
Absorption coefficient	2.561 mm^{-1}
$F(000)$	1336
Data collection	
Diffractometer used	Siemens $R3m/V$
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)
Temperature (K)	294
Monochromator	Highly oriented graphite crystal
2θ Range	4.0–55.0°
Scan type	ω–2θ
Scan speed	Variable; 4.51–14.65°/min in ω
Scan range (ω)	0.70° plus K_α-separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	2 measured every 100 reflections
Index ranges	$0 < h < 30$, $1 < k < 12$, $0 < l < 14$
Reflections collected	2833
Independently reflections	2770
Observed reflections	2421 ($F > 4.0\sigma(F)$)
Solution and refinement	
System used	Siemens SHELXTL PLUS (Release 4.1)
Solution	Heavy-atom methods
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$
Hydrogen atoms	Riding model, common refined U (0.10 Å^2)
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
Number of parameters refined	253
Final R indices (obs. data)	$R = 3.87\%$, $wR = 4.96\%$
R indices (all data)	$R = 6.27\%$, $wR = 7.62\%$
Goodness-of-fit	1.30
Largest and mean Δ/σ	0.091, 0.007
Data-to-parameter ratio	9.6 : 1
Largest difference peak	0.77 eÅ^3 (0.73 Å far from Sn)

from the ideal tetrahedral angle (109.47°) of 18.0 and 19.5° for the S–Sn–S "bite" angles. The mean value is larger than the value of 84° in the pentacoordinate complex diphenylchlorotin toluenedithiolate anion [18]. On the other hand two short intramolecular contacts are observed, Sn(1) ··· S(5) (3.19 Å) and Sn(2) ··· S(6)

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U^a
Sn(1)	370(1)	1551(1)	0	59(1)
Sn(2)	1201(1)	2594(1)	2971(1)	58(1)
S(1)	538(1)	−590(2)	1035(2)	67(1)
S(2)	930(1)	827(2)	−1720(2)	75(1)
S(3)	1479(1)	922(3)	4551(2)	75(1)
S(4)	1841(1)	1523(2)	1557(2)	63(1)
S(5)	153(1)	2198(2)	2845(2)	60(1)
S(6)	836(1)	3761(2)	641(2)	54(1)
C(1)	−481(5)	2133(12)	−449(15)	93(4)
C(2)	1404(6)	4599(10)	3629(11)	89(4)
C(3)	1078(4)	−1262(7)	41(9)	61(2)
C(4)	1351(4)	−2475(8)	449(11)	70(3)
C(5)	1761(5)	−3081(10)	−247(13)	85(4)
C(6)	1919(5)	−2527(11)	−1346(17)	98(5)
C(7)	1664(6)	−1315(10)	−1784(13)	87(4)
C(8)	1230(4)	−675(8)	−1070(9)	64(3)
C(9)	1917(4)	−179(9)	3667(8)	64(3)
C(10)	2133(6)	−1339(10)	4241(9)	81(4)
C(11)	2496(6)	−2240(11)	3621(12)	84(4)
C(12)	2637(5)	−2003(12)	2414(12)	88(4)
C(13)	2436(4)	−836(9)	1812(9)	68(3)
C(14)	2072(4)	78(7)	2443(7)	57(2)
C(15)	−78(3)	3838(7)	2288(7)	53(2)
C(16)	−573(4)	4397(8)	2762(7)	62(3)
C(17)	−777(4)	5655(9)	2303(9)	67(3)
C(18)	−475(5)	6343(8)	1420(9)	72(3)
C(19)	20(4)	5768(8)	918(8)	61(2)
C(20)	216(4)	4504(7)	1330(7)	54(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

(2.90 Å); these are greater than the sum of the covalent radii (2.44 Å) but well below the sum of the Van der Waals radii (4.05 Å [16]). These distances are comparable with the intermolecular Sn · · · S contact observed in the 2,2-dimethyl-1,3,2-dithiastannolane (3.182 Å), which is considered to complete the five-coordination at Sn [9]. Moreover in the 2,2-dibutyl-1,3,2-dithiastannolane the two intermolecular Sn · · · S distances (3.69 Å) were described as reflecting weak coordination at the tin [10]. Sn · · · S intramolecular interaction was also observed in the structure of α-sulphur-substituted organotin compounds, with contact distances between 3.08 and 3.29 Å [19]. Thus we believe that the two tin atoms may be better described as penta-coordinate in a severely distorted trigonal bipyramidal geometry. In the first bipyramid S(1), S(2) and S(5) form the equatorial plane, with Sn(1) at +0.57 Å and apical C(1) and S(6) at +2.55 and −0.84 Å, respectively. In the second, S(3), S(4) and S(6) are equatorial with Sn(2) out of plane of +0.34 Å and apical C(2) and S(5) at +2.31 and −1.38 Å, respectively. The geometrical differences between the two bipyramids are probably attributable to packing effects and intermolecular strain.

The Sn(1) · · · S(4) and Sn(2) · · · S(1) distances (3.81 and 4.03 Å respectively) are also smaller than the sum of the Van der Waals radii, but they can hardly be

Table 3

Selected bond lengths (Å) and angles (°) with esd's in parentheses

Sn(1)-S(1)	2.386(2)	Sn(2)-S(3)	2.443(3)
Sn(1)-S(2)	2.381(3)	Sn(2)-S(4)	2.374(2)
Sn(1)-C(1)	2.11(1)	Sn(2)-C(2)	2.12(1)
Sn(1)-S(6)	2.493(2)	Sn(2)-S(5)	2.435(2)
S(1)-C(3)	1.78(1)	S(4)-C(14)	1.78(1)
S(2)-C(8)	1.76(1)	S(5)-C(15)	1.78(1)
S(3)-C(9)	1.76(1)	S(6)-C(20)	1.77(1)
S(1)-Sn(1)-S(2)	91.5(1)	S(3)-Sn(2)-S(4)	90.0(1)
S(1)-Sn(1)-C(1)	119.5(3)	S(3)-Sn(2)-C(2)	108.0(3)
S(1)-Sn(1)-S(6)	122.7(1)	S(3)-Sn(2)-S(5)	101.3(1)
S(2)-Sn(1)-C(1)	114.1(4)	S(4)-Sn(2)-C(2)	118.5(4)
S(2)-Sn(1)-S(6)	103.5(1)	S(4)-Sn(2)-S(5)	120.9(1)
C(1)-Sn(1)-S(6)	104.0(3)	C(2)-Sn(2)-S(5)	112.4(4)
Sn(1)-S(6)-C(20)	96.5(2)	Sn(2)-S(5)-C(15)	100.2(3)
S(6)-C(20)-C(15)	121.5(5)	S(5)-C(15)-C(20)	121.1(6)
Sn(1)-S(1)-C(3)	98.4(3)	Sn(2)-S(3)-C(9)	99.8(3)
Sn(1)-S(2)-C(8)	98.3(3)	Sn(2)-S(4)-C(14)	100.4(3)
S(1)-C(3)-C(8)	124.1(6)	S(3)-C(9)-C(14)	124.1(6)
C(3)-C(8)-S(2)	126.2(7)	C(9)-C(14)-S(4)	125.1(6)

regarded as reflecting intramolecular associations since the geometry about the tin atoms provides no indication of an octahedral arrangement.

The Sn(1) · · · S(5) and Sn(2) · · · S(6) interactions probably contribute to hold the 1,3-dithiabenzo[*c*]-2-stannolanyl moieties in a nearly eclipsed position (cf. Fig. 2).

Table 4

No.	Plane	Deviations	
(i) Relevant least-squares planes and deviations (Å) of some atoms			
1	C(3)-(8)	S(1) −0.02; S(2) −0.02; Sn(1) −0.32	
2	C(3)-(14)	S(3) 0.03; S(4) 0.01; Sn(2) −0.16	
3	C(15)-(20)	S(5) −0.03; S(6) −0.09; Sn(1) −2.18; Sn(2) 1.58	
4	S(1), C(3), C(8), S(2)	Sn(1) 0.36; S(6) 2.62; C(1) −0.91	
5	S(3), C(9), C(14), C(4)	Sn(2) −0.21; S(5) −2.41; C(2) 1.37	
(ii) Dihedral angles (°)			
(1)-(2)	10.7	(1)-(4)	0.8
(1)-(3)	16.3	(2)-(5)	0.9
(2)-(3)	26.6	(4)-(5)	11.8
(iii) Torsion angles (°)			
Sn(1)-S(1)-C(3)-C(8)	−8.9	Sn(2)-S(3)-C(9)-C(14)	6.2
S(1)-C(3)-C(8)-S(2)	0.2	S(3)-C(9)-C(14)-S(4)	−1.8
C(3)-C(8)-S(2)-Sn(1)	8.7	C(9)-C(14)-S(4)-Sn(2)	−4.0
C(8)-S(2)-Sn(1)-S(1)	−10.3	C(14)-S(4)-Sn(2)-S(3)	5.6
S(2)-Sn(1)-S(1)-C(3)	10.4	S(4)-Sn(2)-S(3)-C(9)	−6.3
C(1)-Sn(1)-S(6)-C(20)	34.3	C(20)-C(15)-S(5)-Sn(2)	44.5
Sn(1)-S(6)-C(20)-C(15)	57.4	C(15)-S(5)-Sn(2)-C(2)	39.7
S(6)-C(20)-C(15)-S(5)	−0.8		

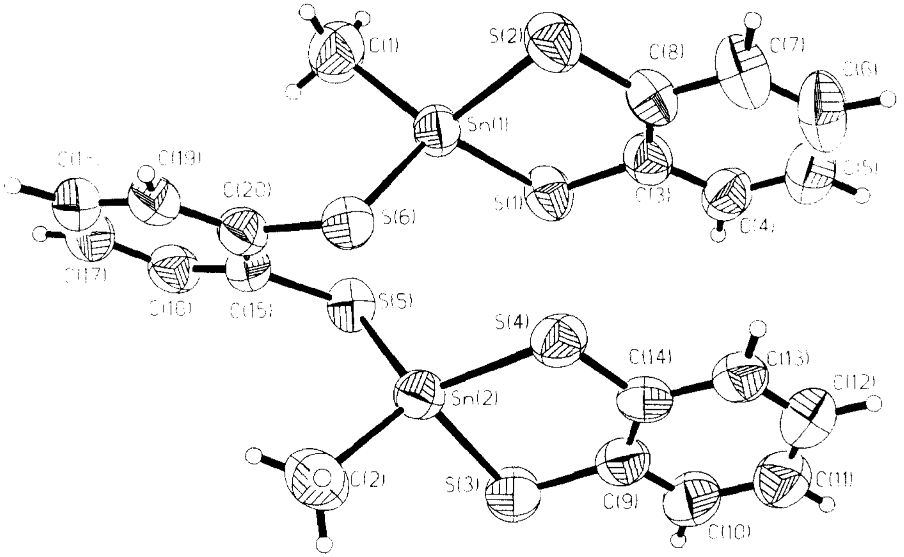

Fig. 1. The structure of [1,2-benzenedithiolate(2 –)-*S*, *S*′]-bis{2-methyl-1,3-dithiabenzo[*c*]-2-stannolanyl} with thermal ellipsoids at the 50% level. H atoms are represented by spheres of arbitrary size.

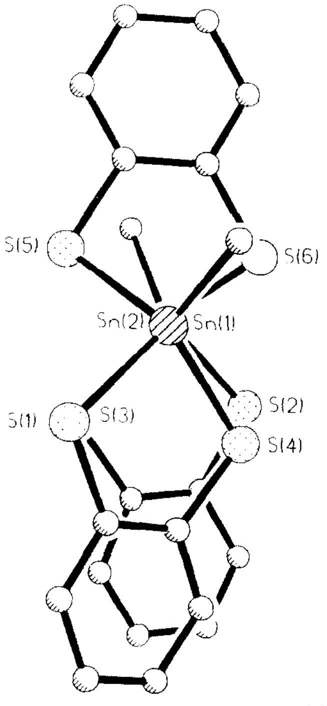

Fig. 2. Projection of [1,2-benzendithiolate(2–)-*S*, *S*′]-bis{2-methyl-1,3-dithiabenzo[*c*]-2-stannolanyl} down the Sn(1) · · · Sn(2) axis. S(1) is overlapping S(3) and Sn(1) obscures Sn(2).

The three rings are roughly parallel (cf. Table 4, Fig. 2) and the torsion angles for the two five-membered rings C–S–Sn–S–C are close to 0° (maximum departure of 10.4°). The Sn(1) ··· Sn(2) separation is 3.89 Å and the distance between the centroids of C(3)–(8) and C(9)–(14) rings is 4.47 Å.

Other bond lengths and angles do not merit any comment, since they do not differ significantly from the expected values [20], and in the packing of the four molecules in the unit cell no interatomic contacts shorter than the sum of the Van der Waals radii are observed.

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