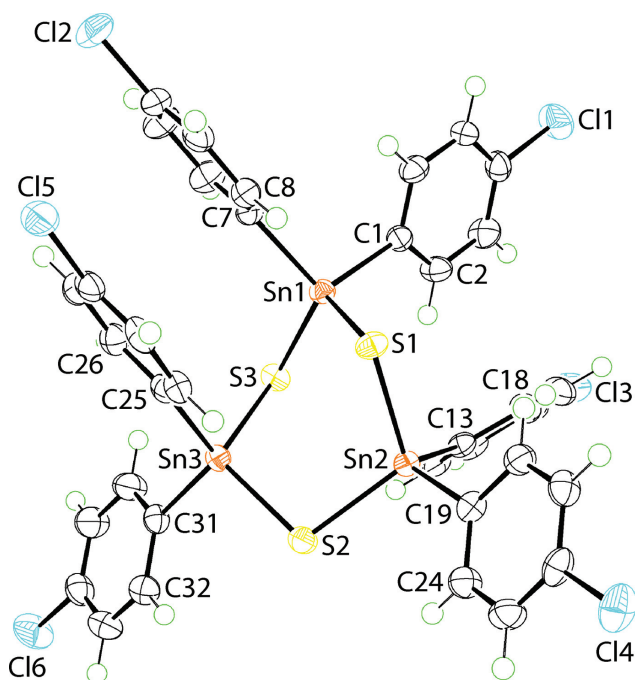


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Crystal structure of 2,2,4,4,6,6-hexakis(4-chlorophenyl)-1,3,5,2,4,6-trithiatristanninane, $C_{36}H_{24}Cl_6S_3Sn_3$



The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.10 × 0.06 × 0.04 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	20.7 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{\max} , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	47327, 6937, 0.032
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6635
$N(\text{param})_{\text{refined}}$:	433
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Sn1	0.24491(2)	0.57778(2)	0.50844(2)	0.01549(4)
Sn2	0.39887(2)	0.75164(2)	0.57769(2)	0.01476(4)
Sn3	0.11603(2)	0.76134(2)	0.45669(2)	0.01582(4)
S1	0.44349(5)	0.64736(3)	0.51161(2)	0.01871(10)
S2	0.27003(5)	0.84020(3)	0.51547(3)	0.02078(11)
S3	0.06039(5)	0.65607(3)	0.52062(2)	0.01856(10)
Cl1	0.27701(6)	0.32391(3)	0.73857(3)	0.03366(13)
Cl2	0.25307(6)	0.38242(3)	0.23951(3)	0.03496(13)
Cl3	0.15921(7)	0.59722(3)	0.83106(3)	0.03782(14)
Cl4	0.98627(5)	0.90130(3)	0.61796(3)	0.03142(13)
Cl5	0.32369(6)	0.59405(3)	0.20036(3)	0.03229(13)
Cl6	-0.44251(6)	0.94468(3)	0.41901(3)	0.03753(14)
C1	0.24760(19)	0.49902(11)	0.58427(10)	0.0171(4)
C2	0.2009(2)	0.51276(12)	0.64398(11)	0.0224(4)
H2	0.162880	0.559311	0.652039	0.027*
C3	0.2091(2)	0.45924(13)	0.69186(11)	0.0253(5)
H3	0.175545	0.468477	0.732120	0.030*
C4	0.2673(2)	0.39214(12)	0.67979(11)	0.0219(4)
C5	0.3158(2)	0.37760(12)	0.62154(11)	0.0215(4)
H5	0.356781	0.331707	0.614212	0.026*
C6	0.3040(2)	0.43088(12)	0.57374(11)	0.0203(4)

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Abstract

$C_{36}H_{24}Cl_6S_3Sn_3$, monoclinic, $P2_1/c$ (no. 14), $a = 10.3180(1)$ Å, $b = 18.1008(1)$ Å, $c = 20.9015(2)$ Å, $\beta = 94.536(10)^\circ$, $V = 3891.42(6)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0177$, $wR_{\text{ref}}(F^2) = 0.0448$, $T = 100(2)$ K.

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H6	0.335062	0.420578	0.533085	0.024*
C7	0.2455(2)	0.51760(11)	0.42087(10)	0.0182(4)
C8	0.3559(2)	0.51690(12)	0.38639(11)	0.0203(4)
H8	0.429800	0.545233	0.401233	0.024*
C9	0.3593(2)	0.47529(12)	0.33059(11)	0.0220(4)
H9	0.434786	0.474989	0.307319	0.026*
C10	0.2513(2)	0.43444(12)	0.30961(11)	0.0239(5)
C11	0.1408(2)	0.43345(13)	0.34316(12)	0.0284(5)
H11	0.067519	0.404598	0.328438	0.034*
C12	0.1391(2)	0.47541(13)	0.39873(11)	0.0254(5)
H12	0.063593	0.475191	0.421985	0.030*
C13	0.31780(19)	0.70915(11)	0.66075(10)	0.0170(4)
C14	0.1899(2)	0.72169(12)	0.67542(10)	0.0187(4)
H14	0.135453	0.753398	0.648942	0.022*
C15	0.1417(2)	0.68813(12)	0.72850(11)	0.0221(4)
H15	0.054910	0.696919	0.738596	0.027*
C16	0.2219(2)	0.64185(12)	0.76630(11)	0.0252(5)
C17	0.3506(2)	0.63001(13)	0.75447(11)	0.0264(5)
H17	0.405222	0.599422	0.781936	0.032*
C18	0.3977(2)	0.66406(12)	0.70139(11)	0.0223(4)
H18	0.485625	0.656576	0.692554	0.027*
C19	0.58702(19)	0.79940(12)	0.59291(10)	0.0178(4)
C20	0.6968(2)	0.75462(12)	0.60179(11)	0.0215(5)
H20	0.687298	0.702438	0.602809	0.026*
C21	0.8204(2)	0.78597(13)	0.60918(11)	0.0225(4)
H21	0.895416	0.755580	0.615149	0.027*
C22	0.8320(2)	0.86194(13)	0.60768(10)	0.0221(4)
C23	0.7246(2)	0.90740(13)	0.59840(12)	0.0253(5)
H23	0.734535	0.959543	0.597100	0.030*
C24	0.6019(2)	0.87565(12)	0.59101(11)	0.0221(4)
H24	0.527300	0.906346	0.584585	0.027*
C25	0.1865(2)	0.71137(12)	0.37349(10)	0.0180(4)
C26	0.1034(2)	0.66423(12)	0.33656(11)	0.0213(4)
H26	0.017199	0.656828	0.348196	0.026*
C27	0.1444(2)	0.62807(13)	0.28329(11)	0.0241(5)
H27	0.087121	0.596487	0.258169	0.029*
C28	0.2710(2)	0.63913(13)	0.26755(10)	0.0237(5)
C29	0.3559(2)	0.68476(13)	0.30317(11)	0.0232(5)
H29	0.442317	0.691314	0.291543	0.028*
C30	0.3136(2)	0.72109(12)	0.35633(11)	0.0200(4)
H30	0.371376	0.752691	0.381119	0.024*
C31	-0.06041(19)	0.82310(12)	0.44495(10)	0.0185(4)
C32	-0.0630(2)	0.89982(12)	0.44359(11)	0.0215(4)
H32	0.016478	0.926535	0.448321	0.026*
C33	-0.1793(2)	0.93794(13)	0.43547(12)	0.0250(5)
H33	-0.180298	0.990401	0.434157	0.030*
C34	-0.2947(2)	0.89801(13)	0.42925(11)	0.0249(5)
C35	-0.2952(2)	0.82229(13)	0.43206(13)	0.0291(5)
H35	-0.375080	0.795905	0.428775	0.035*
C36	-0.1778(2)	0.78463(13)	0.43976(13)	0.0276(5)
H36	-0.177393	0.732189	0.441511	0.033*

Source of material

Tetra(4-chlorophenyl)tin was synthesized from the reaction of stannic chloride (Fluka) with 4-chlorophenylmagnesium

bromide (Fluka) in a 1:4 molar ratio. Subsequently, di(4-chlorophenyl)tin dichloride was synthesized from the disproportionation reaction of tetra(4-chlorophenyl)tin with stannic chloride (Fluka) in a 1:1 molar ratio to obtain a white precipitate. The dithiocarbamate ligand was prepared in situ (methanol) from the reaction of carbon disulfide (Merck, 0.02 mL, 0.25 mmol) with di-*n*-butylamine (Merck, 0.04 mL, 0.25 mmol) and NaOH (0.02 mL; 50% w/v); carbon disulfide was added dropwise into the methanol solution (10 mL). The resulting mixture solution was kept at 273 K for 0.5 h. Di(4-chlorophenyl)tin dichloride in methanol (10 mL) was added in the solution and the resulting mixture was stirred for 3 h. The filtrate was evaporated until a white precipitate was obtained. The precipitate was washed with *n*-hexane and recrystallized from dimethyl sulfoxide. The title compound was the side-product from the recrystallization of the precipitate.

Yield: 0.10 g (9%). **M.pt** (Mel-temp II digital melting point apparatus): 339–401 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm⁻¹): 1471 (m) ν(C–C); 782 (m) ν(C–Cl); 604 (w) ν(Sn–C); 450 w ν(Sn–S). **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer, chemical shifts relative to Me₄Si, CDCl₃ solution at 40 °C; ppm): 6.94–7.08 (m, Phenyl-H). **¹³C{¹H} NMR** (as for ¹H NMR): 121.4, 122.4, 124.3, 124.8, 127.4, 133.0 (Ph–C).

Experimental details

The hydrogen atoms were geometrically placed (C–H = 0.95 Å) and refined as riding with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Comment

Crystal structure determinations of cyclic, trinuclear molecules of the general formula [R₂SnS]₃ are comparatively rare. With the exception of the R = CH₂CH₂C(=O)OEt derivative [5], the only other crystallographically characterised species is that with R = Me but, in four polymorphic forms. Thus, tetragonal *P*₄₁, *Z* = 1 [6] and *P*₄₁2₁2, *Z* = 0.5 [7] are known as well as two monoclinic forms *P*₂₁/*c*, *Z* = 1 [8] and *P*₂₁/*n*, *Z* = 2 [9]. The common feature of the structures is the presence of a twisted-boat conformation of the six-membered Sn₃S₃ ring. The title compound, with R = 4-ClC₆H₄, (I), was isolated as a side-product during a course of studies of organotin dithiocarbamates [10, 11]. Herein the crystal structure of (I) is described along with an analysis of the calculated Hirshfeld surfaces.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids) and lacks symmetry. The Sn₃S₃ ring adopts a twisted-boat conformation as is usually observed for molecules of this type [5–9]. In this description, S2 atom is

to a first approximation co-planar with the plane through the three Sn atoms, lying 0.1425(6) Å out of the plane. The S1 and S3 atoms lie to either side of the Sn₃ plane by 1.3639(5) Å, in the same direction as the S2 atom, and 1.4709(5) Å, respectively. Within the ring, the angles subtended at the Sn atoms range from 109.644(18)°, for S1–Sn2–S2, to 111.667(18)°, for S1–Sn3–S3. The angles at the S atoms are narrower, ranging from 100.435(18)°, for Sn1–S3–Sn3, to 103.050(18)°, for Sn1–S1–Sn2. The Sn–S bond lengths span a relatively narrow range, i.e. 2.3989(5) Å, for Sn2–S2, to 2.4221(5) Å, for Sn3–S3. The Sn-atom geometries are approximately tetrahedral based on C₂S₂ donor sets. The widest range of tetrahedral angles of 15.5° is found for the Sn2 atom, i.e. 101.02(6)°, for S1–Sn2–C19, to 116.54(6)°, for S2–Sn2–C13.

In the molecular packing of (I), Sn...Cl [Sn3...Cl3ⁱ = 3.7193(7) Å for symmetry operation (i): $x, 3/2 - y, -1/2 + z$] secondary bonding interactions [12, 13] are apparent. These lead to supramolecular, zig-zag chains, being propagated by glide plane symmetry. Stacking interactions contribute to stability of the chains [Cg(C13–C18)...Cg(C25–C30)ⁱⁱ: 3.5368(13) Å, angle of inclination = 1.37(11)° and off-set = 1.45 Å for (ii): $x, 3/2 - y, 1/2 + z$]. The chains are linked by phenyl-C–H...S contacts [C6–H6...S1ⁱⁱⁱ: H6...S1ⁱⁱⁱ = 2.82 Å, C6...S1ⁱⁱⁱ = 3.565(2) Å with angle at H6 = 136° for (iii) $1 - x, 1 - y, 1 - z$] into a supramolecular layer in the bc-plane. Additional links between chains are of the type Cl...π(phenyl) [C4–Cl1...Cg(C19–C24)^{iv}: Cl1...Cg(C19–C24)^{iv} = 3.3654(11) Å with angle at Cl1 = 132.58(8)° for (iv): $1 - x, -1/2 + y, 3/2 - z$]. The connections between layers to consolidate the three-dimensional architecture are of the type π...π [Cg(C19–C24)...Cg(C31–C35)^v: 3.7131(13) Å, angle of inclination = 1.32(11)° and off-set = 1.16 Å for (v): $1 + x, y, z$] and Cl...π [Cl10–Cl2...Cg(C31–C36)^{vi}: Cl2...Cg(C31–C36)^{vi} = 3.7394(12) Å with angle at Cl2 = 150.79(8)° for (vi): $-x, -1/2 + y, 1/2 - z$].

To analyse the molecular packing, the Hirshfeld surface was calculated as were full- and delineated two-dimensional Fingerprint plots with the aid of Crystal Explorer 17 [14] and standard protocols [15]. This analysis shows the Sn...Cl secondary bonding interactions only make a very minor contribution to the overall surface contacts, i.e. 0.6%. More significant contacts involving Cl are Cl...H/H...Cl, Cl...C/C...Cl, Cl...S/S...Cl and Cl...Cl contacts, making contributions of 28.3, 8.7, 1.6 and 3.8%, respectively. The S atoms also contribute to other surface contacts: S...H/H...S [6.2%] and S...C/C...S [0.5%]. More significant contributions are made

by C...H/H...C [15.4%], C...C [4.9%] and, especially, H...H [30.0%] contacts.

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