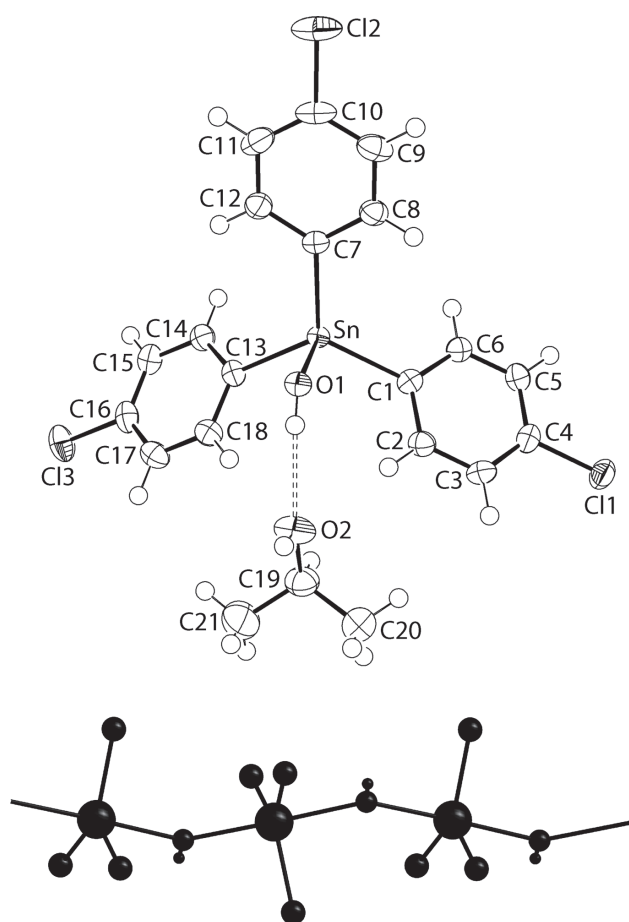


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Crystal structure of *catena*-poly[tri(4-chlorophenyl)-(μ_2 -hydroxido)tin(IV)] – 2-propanol (1/1), $C_{21}H_{21}Cl_3O_2Sn$



Abstract

$C_{21}H_{21}Cl_3O_2Sn$, monoclinic, $P2_1/n$ (no. 14), $a = 13.3360(1)$ Å, $b = 8.2332(1)$ Å, $c = 20.2443(2)$ Å, $\beta = 104.070(1)^\circ$, $V = 2156.10(4)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0199$, $wR_{ref}(F^2) = 0.0544$, $T = 100(2)$ K.

CCDC no.: 1951436

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:	0.16 × 0.07 × 0.03 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ :	13.0 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	49159, 3845, 0.036
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3647
$N(param)_{refined}$:	252
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined using a Mel-temp II digital melting point apparatus and was uncorrected. The IR spectrum was obtained on a Perkin-Elmer RX1 spectrophotometer in a Nujol mull between KBr plates from 4000 to 400 cm⁻¹.

Tetra(4-chlorophenyl)tin was prepared from the reaction of stannic chloride (Fluka) and 4-chlorophenylmagnesium bromide (Fluka) in a 1:4 molar ratio. Tetra(4-chlorophenyl)tin (3.40 g, 6 mmol) was dissolved in dimethylformamide (30 mL) and cooled to 273 K in an ice-salt bath. A chilled dimethylformamide solution (5 mL) of bromine (0.97 g, 6 mmol) was added drop-wise into the solution. When the addition was complete, the mixture was stirred at room temperature for 3 h and a 10% sodium hydroxide solution

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

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Sn	0.74641(2)	0.62820(2)	0.25099(2)	0.01366(6)
Cl1	0.85701(4)	0.45614(6)	0.58296(2)	0.02580(11)
Cl2	1.14436(5)	0.86190(7)	0.12846(4)	0.04162(15)
Cl3	0.29619(4)	0.47006(6)	0.03131(2)	0.03108(12)
O1	0.70141(10)	0.87677(13)	0.26734(7)	0.0165(3)
H1O	0.6489(13)	0.881(3)	0.2829(12)	0.025*
C1	0.78181(13)	0.5769(2)	0.35770(9)	0.0165(3)
C2	0.72610(15)	0.6470(2)	0.40081(10)	0.0202(4)
H2	0.6720	0.7214	0.3826	0.024*
C3	0.74872(16)	0.6094(2)	0.46977(10)	0.0222(4)
H3	0.7101	0.6568	0.4985	0.027*
C4	0.82802(14)	0.5023(2)	0.49600(9)	0.0201(4)
C5	0.88599(14)	0.4329(2)	0.45525(9)	0.0201(4)
H5	0.9410	0.3606	0.4741	0.024*
C6	0.86223(13)	0.4710(2)	0.38622(9)	0.0181(4)
H6	0.9017	0.4237	0.3579	0.022*
C7	0.87130(13)	0.7107(2)	0.21065(9)	0.0158(3)
C8	0.96992(14)	0.7304(2)	0.25384(9)	0.0217(4)
H8	0.9797	0.7115	0.3013	0.026*
C9	1.05356(15)	0.7768(2)	0.22895(10)	0.0270(4)
H9	1.1200	0.7897	0.2588	0.032*
C10	1.03870(16)	0.8041(2)	0.15984(11)	0.0268(4)
C11	0.94273(16)	0.7860(2)	0.11552(10)	0.0279(4)
H11	0.9337	0.8056	0.0682	0.033*
C12	0.85949(14)	0.7388(2)	0.14113(9)	0.0217(4)
H12	0.7934	0.7255	0.1108	0.026*
C13	0.60105(13)	0.5794(2)	0.18139(9)	0.0171(3)
C14	0.50882(15)	0.6493(2)	0.18890(10)	0.0206(4)
H14	0.5103	0.7214	0.2258	0.025*
C15	0.41476(16)	0.6150(2)	0.14327(11)	0.0232(4)
H15	0.3524	0.6619	0.1491	0.028*
C16	0.41373(14)	0.5117(2)	0.08945(9)	0.0222(4)
C17	0.50345(15)	0.4420(2)	0.08004(9)	0.0222(4)
H17	0.5015	0.3714	0.0426	0.027*
C18	0.59676(14)	0.4767(2)	0.12617(9)	0.0196(4)
H18	0.6587	0.4294	0.1198	0.024*
O2	0.52056(12)	0.88333(16)	0.32963(9)	0.0302(3)
H2O	0.507(2)	0.9835(14)	0.3316(14)	0.045*
C19	0.44785(16)	0.7908(3)	0.35541(11)	0.0300(4)
H19	0.4620	0.6733	0.3490	0.036*
C20	0.4606(2)	0.8188(5)	0.43005(13)	0.0641(9)
H20A	0.5318	0.7936	0.4544	0.096*
H20B	0.4129	0.7484	0.4467	0.096*
H20C	0.4455	0.9326	0.4379	0.096*
C21	0.33907(19)	0.8250(4)	0.31621(14)	0.0518(7)
H21A	0.3217	0.9383	0.3234	0.078*
H21B	0.2914	0.7527	0.3320	0.078*
H21C	0.3331	0.8065	0.2676	0.078*

was added drop-wise until a white precipitate was formed. The solid was filtered and recrystallised from 2-propanol to afford the title compound as colourless crystals. Yield: 0.30 g (10%). M.pt: 431–433 K. IR (cm⁻¹) 1568 (m) ν(C–C), 1090 (s) ν(C–O), 1010 (s) ν(C–O), 481 (w) ν(Sn–O).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C). The O-bound H-atoms were located in a difference Fourier map but were refined with a distance restraint of O–H = 0.84 ± 0.01 Å, and with *U*_{iso}(H) set to 1.5*U*_{eq}(O).

Comment

Molecules of the general formula R₃SnOH can be mononuclear as exemplified by R = 2,4,6-Me₃C₆H₂ (mesityl) [5], binuclear, as in the case when R = CF₂CF₃ [6], or polymeric such as when R = Et [7]. While to a first approximation, the adoption of one structural motif over another for R₃SnOH may be attributed to steric effects, well established in organotin chemistry to moderate secondary bonding interactions [8–11], the subtle nature of the adoption of one motif over another is nicely illustrated in the case when R = Ph. Thus, the structure of Ph₃SnOH was established long ago as being polymeric [12] but, when this is co-crystallised with 2,6-bis(1H-benzimidazol-2-yl)pyridine and water [13], it is mononuclear. Herein, the crystal and molecular structures of the R = 4-ClPh derivative, isolated as a 1:1 isopropanol solvate, that is (4-ClPh)₃Sn(OH)·iPrOH, (I), are described.

The crystallographic asymmetric unit of (I) is shown in the upper part of the figure (70% probability displacement ellipsoids). From symmetry, and as indicated in the lower view of the figure (only ipso-C atoms of the 4-ClPh substituents are shown and the solvent molecules are omitted), the solid-state structure of (I) is a one-dimensional coordination polymer with helical symmetry, being propagated along the *b*-axis by 2₁-screw symmetry. The tin atom is therefore coordinated by two hydroxy-O atoms and three ipso-C atoms of the organic substituents. While, the Sn–C bond lengths are experimentally equivalent, that is, [2.1363(17) Å, for Sn–C7, to 2.1393(17) Å, for Sn–C13], there is a disparity in the Sn–O1 bond lengths with the formally covalent Sn–O1 bond length of 2.1805(11) Å being significantly shorter than the formally intermolecular Sn–O1ⁱ bond length of 2.2434(11) Å; symmetry operation (i): 3/2 – x, –1/2 + y, 1/2 – z. As the O1 atoms are approximately *trans* to each other, the O1–Sn–O1ⁱ bond angle is 177.51(2)°, the resultant C₃O₂ coordination geometry is close to trigonal-bipyramidal.

As indicated in the upper view of the figure, the connection between the constituents of the asymmetric unit is a tin-hydroxy-O–H···O(2-propanol) hydrogen bond [O1–H1o···O2: H1o···O2 = 2.148(19) Å, O1···O2 = 2.981(2) Å with angle at H1o = 176(2)°]. The acidic proton of the solvent iPrOH molecule is engaged in an intra-chain 2-propanol–O–H···π(phenyl) interaction [O2–H2o···π(C7–C12)ⁱⁱ: H2o···Cg(C7–C12)ⁱⁱ = 2.353(13) Å, O2···Cg(C7–C12)ⁱⁱ = 3.1203(15) Å with angle at H2o = 151(2)° for symmetry

operation (ii): $3/2 - x$, $1/2 + y$, $1/2 - z$]. Chains pack in the crystal with no directional interactions between them.

To analyse the molecular packing further, using Crystal Explorer 17 [14] and established protocols [15], Hirshfeld surface calculations were performed along with the full and delineated two-dimensional fingerprint plots. This analysis reveals the importance of $Cl \cdots H/H \cdots Cl$ (32.2%), $H \cdots H$ (30.2%) and $C \cdots H/H \cdots C$ (25.6%) contacts to the calculated Hirshfeld surface but, these occur at distances generally greater than the sum of the respective van der Waals radii. The next most important contacts are of the type $C \cdots C$, contributing 3.8%.

As indicated above, there are several polymeric precedents for the one-dimensional coordination polymer found in (I). Zig-zag chains are found in the $R = Et$ derivative [7] and in the mixed species, $Ph_2(Cy)SnOH$ [16], each of which sees the chain having mirror symmetry. Helical chains propagated by 2_1 screw axes are found when $R = Ph$ [12], $R = CH_2Ph$ [17] and in the mixed species $Me_2(PhCH_2)SnOH$ [18]. The discussion of these structures would be incomplete without mentioning the structural analyses of the $R = Me$ derivative, which has attracted considerable attention [19]. Since the original room temperature analysis where a helical chain was shown [20], in a subsequent study, $\{Me_3Sn(OH)\}_n$ was modelled as a 32-fold superstructure with 8_3 -helical chains [21]. At 220 K, the structure has been described as an eight-fold superstructure, with distorted zig-zag chains [22].

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