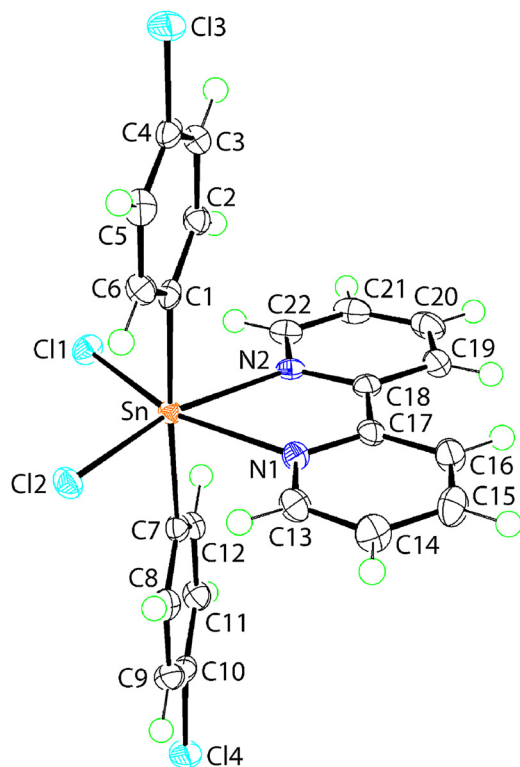


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Crystal structure of dichlorido-bis(4-chlorophenyl- κC^1)(2,2'-bipyridyl- $\kappa^2 N, N'$)tin(IV), $C_{22}H_{16}Cl_4N_2Sn$



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Abstract

$C_{22}H_{16}Cl_4N_2Sn$, monoclinic, $P2_1/n$ (no. 14), $a = 10.0393(1)$ Å, $b = 14.4490(2)$ Å, $c = 14.1502(2)$ Å, $\beta = 92.846(1)^\circ$, $V = 2050.07(5)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0224$, $wR_{ref}(F^2) = 0.0590$, $T = 100$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.13 × 0.10 × 0.06 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	14.8 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	25,880, 3647, 0.036
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3497
$N(param)_{refined}$:	262
Programs:	Bruker [1], SHELX [2, 3], WinGX/ ORTEP [4]

of the atoms including atomic coordinates and displacement parameters.

Source of material

The (4-chlorophenyl)₂SnCl₂ precursor was prepared as per the literature procedure [5]. Equimolar quantities of (4-chlorophenyl)₂SnCl₂ (0.5 g, 1.2 mmol) and 2,2'-bipyridyl (Sigma, 0.2 g, 1.2 mmol) were dissolved separately in ethanol (50 mL). The solutions were mixed to give a white precipitate which was recrystallised from methanol to afford colourless crystals of the title compound. Yield: 0.41 g (60.1%). **M.pt** (Stuart SMP30 digital melting point apparatus; uncorrected): 509–511 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm⁻¹): 1600(s) $\nu(C=N)$, 1594 (m) $\nu(C=C)$, 1084 (m) $\nu(C-N)$. ¹H NMR (Bruker Ascend 400 MHz NMR spectrometer; DMSO-*d*₆; ppm relative to Me₄Si): δ 7.40–7.47 (m, 4H, Ph-H), 7.62–7.67 (m, 4H, Ph-H), 7.70–7.75 (m, 6H, Pyr-H), 8.21–8.28 (m, 2H, Pyr-H). ¹³C{¹H} NMR (as for ¹H NMR): 121.6, 123.4, 128.8, 129.8, 134.3, 136.9, 138.9, 148.9, 157.4.

Experimental details

The H atoms were geometrically placed (C–H = 0.95 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. Owing to poor agreement, seven reflections (as detailed in the deposited CIF) were omitted from the final cycles of refinement.

Comment

Having the attributes of hydrogen-bonding, for example, directionality and strength, halogen-bonding is well-

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

Atom	x	y	z	U _{iso} [*] /U _{eq}
Sn	0.48922 (2)	0.34213 (2)	0.34646 (2)	0.00959 (7)
Cl1	0.35554 (6)	0.44407 (4)	0.44585 (4)	0.01527 (14)
Cl2	0.73368 (6)	0.36947 (5)	0.38890 (4)	0.01501 (14)
Cl3	0.49888 (7)	0.66403 (5)	0.00763 (5)	0.01858 (15)
Cl4	0.48966 (7)	0.00721 (5)	0.67177 (5)	0.01939 (15)
N1	0.5352 (2)	0.22738 (16)	0.23146 (15)	0.0120 (5)
N2	0.2884 (2)	0.28155 (16)	0.27707 (15)	0.0114 (4)
C1	0.4930 (3)	0.44484 (19)	0.23635 (18)	0.0117 (5)
C2	0.3745 (3)	0.48319 (19)	0.19884 (18)	0.0135 (5)
H2	0.292026	0.463369	0.222010	0.016*
C3	0.3748 (3)	0.5503 (2)	0.12777 (18)	0.0144 (6)
H3	0.293527	0.575887	0.102478	0.017*
C4	0.4957 (3)	0.57877 (19)	0.09485 (18)	0.0145 (6)
C5	0.6149 (3)	0.5425 (2)	0.13087 (19)	0.0162 (6)
H5	0.697138	0.563035	0.107763	0.019*
C6	0.6131 (3)	0.4756 (2)	0.20149 (19)	0.0142 (6)
H6	0.694846	0.450346	0.226428	0.017*
C7	0.4888 (3)	0.23218 (19)	0.44930 (18)	0.0125 (5)
C8	0.6047 (3)	0.1833 (2)	0.47377 (19)	0.0152 (6)
H8	0.684796	0.198237	0.444123	0.018*
C9	0.6055 (3)	0.1131 (2)	0.54082 (19)	0.0158 (6)
H9	0.685144	0.079962	0.557020	0.019*
C10	0.4880 (3)	0.09214 (19)	0.58364 (18)	0.0142 (6)
C11	0.3709 (3)	0.1393 (2)	0.56072 (19)	0.0154 (6)
H11	0.291089	0.124002	0.590499	0.019*
C12	0.3720 (3)	0.2093 (2)	0.49344 (19)	0.0144 (6)
H12	0.292007	0.242092	0.477280	0.017*
C13	0.6593 (3)	0.2006 (2)	0.21367 (19)	0.0159 (6)
H13	0.732261	0.228985	0.247745	0.019*
C14	0.6852 (3)	0.1330 (2)	0.1473 (2)	0.0189 (6)
H14	0.774118	0.114378	0.137105	0.023*
C15	0.5790 (3)	0.0933 (2)	0.0965 (2)	0.0203 (6)
H15	0.593860	0.047696	0.049885	0.024*
C16	0.4506 (3)	0.1207 (2)	0.1143 (2)	0.0180 (6)
H16	0.376438	0.094166	0.079883	0.022*
C17	0.4312 (3)	0.1878 (2)	0.18311 (18)	0.0127 (5)
C18	0.2954 (3)	0.21638 (19)	0.20850 (18)	0.0129 (5)
C19	0.1812 (3)	0.1775 (2)	0.1660 (2)	0.0170 (6)
H19	0.187879	0.132879	0.117149	0.020*
C20	0.0579 (3)	0.2040 (2)	0.1951 (2)	0.0196 (6)
H20	-0.020962	0.177475	0.166768	0.024*
C21	0.0498 (3)	0.2694 (2)	0.2659 (2)	0.0182 (6)
H21	-0.034149	0.288067	0.287551	0.022*
C22	0.1674 (3)	0.3069 (2)	0.30448 (19)	0.0152 (6)
H22	0.162202	0.352600	0.352434	0.018*

established in crystals of molecules containing halide atoms [6, 7]. In this context and during the course of structural studies of relatively halide-rich diorganotin dichlorides [5, 8, 9], crystals of the title adduct (4-chlorophenyl)₂SnCl₂(2,2'-bipyridyl), hereafter (I), were isolated.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids). The tin atom in (I) is located on a general position and is coordinated by two chloride atoms [Sn–Cl1, Cl2 = 2.4772(6) & 2.5285(6) Å], two nitrogen atoms [Sn–N1, N2 = 2.384(2) & 2.366(2) Å] and two ipso-carbon atoms [Sn–C1, C7 = 2.153(3) & 2.155(3) Å] of the 4-chlorophenyl groups. A significant discrepancy is noted in the Sn–Cl bond lengths with the longer Sn–Cl2 bond being *trans* to the N2 atom, forming the shorter of the Sn–N bonds; the 4-chlorophenyl groups are opposite each other. However, it is noted that previously reported DFT calculations indicated non-systematic variations in the geometric parameters involving tin atom may be generally ascribed to the influence of molecular packing effects, for example for compounds of the general formula R₂SnCl₂(bipyridyl-type ligand) [10, 11]. Although the C₂Cl₂N₂ donor set approximates an octahedron, there are deviations from 180° noted for the *trans* angles, i.e. C1–Sn–C7 is 175.97(10)°, Cl1–Sn–N1 is 158.38(6)° and Cl2–Sn–N2 is 162.43(6)°. These distortions may be ascribed, at least in part, to the tight N1–Sn–N2 chelate angle of 69.47(8)°.

There are several crystal structures related to (I) available in the literature. Thus, the two polymorphs of Ph₂SnCl₂(2,2'-bipyridyl) [12, 13] and that of (4-tolyl)₂SnCl₂(2,2'-bipyridyl) [14] adopt the same structural motif, as does the compound closely related to (I) where 2,2'-bipyridyl is replaced by 1,10-phenanthroline [8].

The most notable interactions in the crystal are of the type chlorophenyl–C–Cl⋯π(pyridyl, chlorophenyl) and π(pyridyl)⋯π(chlorophenyl). For the former interactions, each chloride of the chlorophenyl groups is located in a bay defined by two rings [C4–Cl3⋯Cg(N1–C13–C17)ⁱ: Cl3⋯Cg(N1–C13–C17)ⁱ = 3.5402(13) Å with angle at Cl3 = 169.76(11)°; C4–Cl3⋯Cg(C1–C6)ⁱ: Cl3⋯Cg(C1–C6)ⁱ = 3.5353(13) Å with angle at Cl3 = 88.91(9)°; C10–Cl4⋯Cg(N1–C13–C17)ⁱⁱ: Cl4⋯Cg(N1–C13–C17)ⁱⁱ = 3.4013(13) Å with angle at Cl4 = 171.47(11)°; C10–Cl4⋯Cg(C7–C12)ⁱⁱ: Cl4⋯Cg(C7–C12)ⁱⁱ = 3.6311(13) Å with angle at Cl4 = 86.88(9)° for symmetry operations (i): 1–x, 1–y, –z and (ii): 1–x, –y, 1–z] with the result a supramolecular chain can be discerned along [0 –1 1]. Based on the C–Cl⋯Cg angles, each chloride atom forms an end-on C–Cl⋯π interaction with a pyridyl ring and a side-on C–Cl⋯π interaction with a 4-chlorophenyl ring. The connections between the chains to consolidate a three-dimensional architecture are the π(pyridyl)⋯π(chlorophenyl) contacts [Cg(N2, C18–C22)⋯Cg(C7–C12)ⁱⁱⁱ = 3.7972(16) Å, angle between rings = 11.41(13)° and the slippage = 2.12 Å for (iii): –1/2+x, 1/2–y, –1/2+z].

Additional data on the molecular packing was achieved by the calculation of the Hirshfeld surfaces and two-dimensional fingerprint plots (full and delineated into

individual contacts) with Crystal Explorer 17 [15] using literature procedures [16]. As is usually the case, H...H contacts dominate, at 33.1%. Other significant contributions to the surface contacts are due to Cl...H/H...Cl [29.0%], C...H/H...C [16.3%] and Cl...C/C...Cl [11.5%]. The next most significant contribution comes from Cl...Cl contacts, at 2.0%, but these, e.g. Cl1...Cl1^{iv} = 3.5962(8) Å [(iv): 1-x, 1-y, 1-z] are at distances longer than the van der Waals radii of 3.50 Å [17] and are unlikely to be structure directing. Similar lack of formation of Cl...Cl halogen-bonding interactions was noted for the other aforementioned chloride-rich diorganotin dichloride species [5, 8, 9].

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