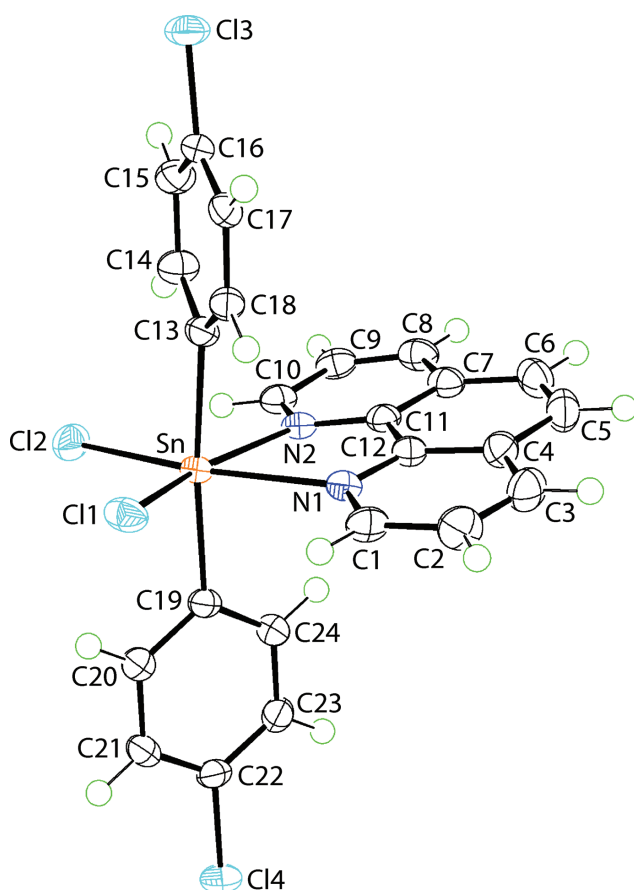DE GRUYTER

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Crystal structure of dichloridobis(4-chlorophenyl-κC^1)(1,10-phenanthroline-κ$^2N,N'$)tin(IV), C$_{24}$H$_{16}$Cl$_4$N$_2$Sn

Abstract

C$_{24}$H$_{16}$Cl$_4$N$_2$Sn, orthorhombic, $Pccn$ (no. 56), $a =$ 19.08967(6) Å, $b =$ 15.87805(5) Å, $c =$ 15.13748(5) Å, $V =$ 4588.27(3) Å^3, $Z =$ 8, $R_{gt}(F) =$ 0.0173, $wR_{ref}(F^2) =$ 0.0474, $T =$ 100(2) K.

CCDC no.: 1978686

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:	$0.14 \times 0.07 \times 0.07$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	13.3 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	102912, 4091, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4073
$N(param)_{refined}$:	280
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

Di(4-chlorophenyl)tin dichloride was prepared from the comproportionation of tetra(4-chlorophenyl)tin (Aldrich; 0.56, 1 mmol) with stannic chloride (Fluka; 0.26 g, 1 mmol). Di (4-chlorophenyl)tin dichloride (0.42 g, 1.0 mmol) and 1,10-phenanthroline (Sigma-Aldrich; 0.18 g, 1.0 mmol) were heated in 95% ethanol (30 mL) for 1 h. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. Yield: 0.33 g (55.7%). **M.pt** (Mel-temp II digital melting point apparatus): 549–551 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 1009 (m) ν(C−N), 488 (m) ν(Sn−N). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer; DMSO-d6; p.p.m. relative to Me$_4$Si): δ 7.31–8.55 (m, 16H, Ph−H). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): δ 127.1, 127.8, 128.8, 129.5, 133.2, 136.6, 137.7, 138.9, 142.0, 149.8 (Ar−C). **^{119}Sn{^{1}H} NMR** (as for ^{1}H NMR; p.p.m. relative to Me$_4$Si): δ −368.1.

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

Atom	x	y	z	U_{iso}*/U_{eq}
Sn	0.22706(2)	0.51890(2)	0.58640(2)	0.01431(5)
Cl1	0.14557(2)	0.39622(3)	0.58969(3)	0.02163(10)
Cl2	0.18798(2)	0.61222(3)	0.70960(3)	0.02360(10)
Cl3	0.43873(2)	0.31486(3)	0.86180(3)	0.02702(11)
Cl4	0.02419(2)	0.72135(3)	0.29899(3)	0.02537(10)
N1	0.28770(8)	0.46193(9)	0.46429(10)	0.0164(3)
N2	0.32458(8)	0.60500(9)	0.55256(10)	0.0161(3)
C1	0.26627(10)	0.39624(13)	0.41674(12)	0.0205(4)
H1	0.222169	0.371488	0.429862	0.025*
C2	0.30657(10)	0.36239(12)	0.34800(13)	0.0262(4)
H2	0.289743	0.315691	0.315006	0.031*
C3	0.37048(11)	0.39722(12)	0.32876(13)	0.0259(4)
H3	0.398375	0.374443	0.282600	0.031*
C4	0.39462(10)	0.46672(12)	0.37750(12)	0.0204(4)
C5	0.46074(11)	0.50664(13)	0.36169(13)	0.0246(4)
H5	0.491023	0.484723	0.317506	0.029*
C6	0.48077(10)	0.57497(13)	0.40858(13)	0.0244(4)
H6	0.525277	0.599672	0.397746	0.029*
C7	0.43557(9)	0.61074(11)	0.47462(12)	0.0194(4)
C8	0.45241(10)	0.68379(12)	0.52239(12)	0.0221(4)
H8	0.496289	0.710673	0.513349	0.027*
C9	0.40553(10)	0.71653(12)	0.58223(11)	0.0206(4)
H9	0.416255	0.766417	0.614121	0.025*
C10	0.34182(10)	0.67498(11)	0.59520(11)	0.0181(4)
H10	0.309440	0.697862	0.636370	0.022*
C11	0.37042(9)	0.57276(11)	0.49229(11)	0.0166(3)
C12	0.35021(9)	0.49849(11)	0.44423(12)	0.0170(3)
C13	0.29970(9)	0.45236(11)	0.66907(12)	0.0165(3)
C14	0.33268(10)	0.49479(12)	0.73795(13)	0.0211(4)
H14	0.324932	0.553490	0.745177	0.025*
C15	0.37653(10)	0.45307(12)	0.79607(12)	0.0219(4)
H15	0.398643	0.482448	0.843095	0.026*
C16	0.38750(9)	0.36773(12)	0.78430(12)	0.0184(4)
C17	0.35729(9)	0.32381(11)	0.71500(12)	0.0174(3)
H17	0.366598	0.265556	0.706848	0.021*
C18	0.31302(9)	0.36685(11)	0.65760(11)	0.0172(3)
H18	0.291633	0.337526	0.610009	0.021*
C19	0.16302(9)	0.58702(11)	0.49497(11)	0.0157(3)
C20	0.09003(9)	0.57909(11)	0.49983(12)	0.0168(3)
H20	0.069742	0.545249	0.544819	0.020*
C21	0.04694(9)	0.62010(11)	0.43966(12)	0.0178(3)
H21	−0.002500	0.613891	0.442545	0.021*
C22	0.07743(9)	0.67024(11)	0.37536(11)	0.0175(3)
C23	0.14931(9)	0.68122(12)	0.36999(12)	0.0195(4)
H23	0.169231	0.716968	0.326380	0.023*
C24	0.19176(9)	0.63844(12)	0.43027(12)	0.0185(4)
H24	0.241187	0.644637	0.426937	0.022*

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C).

Comment

Simple diorganotindihalide adducts with chelating bipyridine-type molecules (NN), i.e. R$_2$SnX$_2$(NN), featured in early geometry optimisation (DFT) studies whereby the experimental structure determined in a crystal was compared with the calculated, gas-phase structure [5, 6]. These investigations demonstrated that non-systematic variations in tin—ligand parameters were the result of the influence of the crystalline environment rather than being due to any chemical reason(s) [5, 6]. In continuation of recent studies in this area [7, 8], herein, the crystal and molecular structures of a new derivative, (4-ClC$_6$H$_4$)$_2$SnCl$_2$(1,10-phenanthroline), (I), are described, complemented by an analysis of the calculated Hirshfeld surfaces.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids). The hexa-coordinated tin atom exists in a distorted octahedral geometry defined by two *trans*-ipso-carbon atoms, derived from the 4-chlorophenyl substituents, two *cis*-chloride atoms and the two nitrogen atoms derived from the chelating 1,10-phenanthroline ligand. In (I), the Sn—Cl bond lengths are experimentally equivalent [Sn—Cl1 = 2.4934(4) Å and Sn—Cl2 = 2.4960(4) Å] as are the two Sn—N bonds [Sn—N1 = 2.3611(15) Å and Sn—N2 = 2.3659(15) Å]. The major distortion from the ideal octahedral geometry is traced to the acute N1—Sn—N2 chelate angle of 70.49(5)°, with the opposite Cl1—Sn—Cl2 angle being 105.214(15)°. In terms of the *trans* angles, the greatest deviation from 180° is 161.21(4)° for Cl1—Sn—N2. The five-membered chelate ring exhibits deviations from planarity [r.m.s. deviation = 0.093 Å] with the deviations to either side of the plane being 0.031(2) Å, for the Cl2 atom, and 0.078(1) Å, for N2.

The most closely related structure available for comparison is the unsusbtituted derivative, i.e. Ph$_2$SnCl$_2$(1,10-phenanthroline) [9]. Here, the Sn—Cl bond lengths are equivalent [Sn—Cl = 2.4487(11) and 2.4563(11) Å] but, the Sn—N bond lengths are experimentally distinct [Sn—N 2.341(3) and 2.379(3) Å].

In the crystal of (I), molecules are linked into supramolecular chains along the *c*-axis (glide-symmetry) being connected by chlorophenyl-C—H⋯π(chlorophenyl) interactions [C15—H15⋯Cg(C19—C24)^i: H15⋯Cg(C19—C24)^i = 2.74 Å, C15⋯Cg(C19—C24)^i = 3.502(2) Å with angle at H15 = 138° for symmetry operation (i) 1/2 − x, y, 1/2 + z]. The chains are connected into a three-dimensional architecture by phenanthroline-C—H⋯Cl(chlorophenyl) [C8—H8⋯Cl3^{ii}: H8⋯Cl3^{ii} = 2.80 Å, C8⋯Cl3^{ii} = 3.4239(19) Å with angle at H8 = 124° for (ii) 1 − x, 1/2 + y, 3/2 − z] and chlorophenyl-C—H⋯Cl(chlorido) [C21—H21⋯Cl1^{iii}: H21⋯Cl1^{iii} = 2.78 Å, C21⋯Cl1^{iii} = 3.7108(18) Å with angle at H21 = 167° for (iii) −x, 1 − y, 1 − z] interactions. Finally, a Cl⋯Cl halogen bond involving the independent chlorophenyl chloride atoms occurs in the inter-column region of the packing [Cl3⋯Cl4^{iv} = 3.2848(6) Å for (iv) 1/2 + x, −1/2 + y, 1 − z].

The calculation of surface contacts for a molecule in a crystal gives additional insight into the molecular packing. Accordingly, the calculated Hirshfeld surfaces and two-dimensional fingerprint plots (full and delineated into individual contacts) were calculated with the Crystal Explorer 17 program [10] as per earlier studies [11]. With four peripheral chloride atoms and from the foregoing discussion of the supramolecular association in the crystal of (I), it is not suprising that $Cl\cdots H/H\cdots Cl$ surface contacts are prominent, contributing 33.0% of all contacts, eclipsing those of the type $H\cdots H$ [29.5%] and $C\cdots H/H\cdots C$ [23.0%]. The remaining 14.5% of contacts comprise $Cl\cdots C/C\cdots Cl$ and $C\cdots C$, each contributing 6.2%, $Cl\cdots Cl$ [2.0%] and $N\cdots H/H\cdots N$ [0.1%].

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