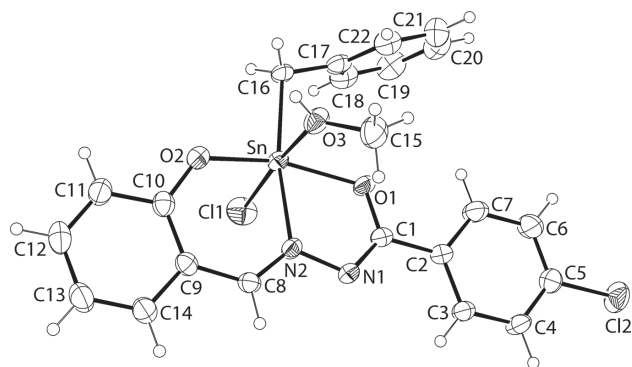See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink*

Crystal structure of benzyl-chlorido-(4-chloro-*N*-[(2-oxidophenyl)methylidene]benzenecarbohydrazonato)-methanol-tin(IV), C$_{22}$H$_{20}$Cl$_2$N$_2$O$_3$Sn

Abstract

C$_{22}$H$_{20}$Cl$_2$N$_2$O$_3$Sn, orthorhombic, $P2_12_12_1$ (no. 19), $a = 8.1234(3)$ Å, $b = 10.7966(3)$ Å, $c = 24.9785(8)$ Å, $V = 2190.74(12)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0271$, $wR_{ref}(F^2) = 0.0645$, $T = 293(2)$ K.

CCDC no.: 1947081

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.

Source of material

The melting point was measured on a Electrothermal digital melting point apparatus and was uncorrected. The elemental analysis was performed on a Perkin-Elmer EA2400 CHN analyser. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrophotometer equipped as a Nujol mull in a KBr cell from 4000 to 400 cm^{-1}. The ^{1}H NMR spectrum was

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	$0.34 \times 0.10 \times 0.08$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.44 mm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX, ω
θ_{max}, completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	22320, 5474, 0.042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5015
$N(param)_{refined}$:	275
Programs:	Bruker [1], SHELX [2–4], WinGX/ORTEP [5]

recorded in DMSO-d_6 solution on a Jeol JNM-ECA 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

Dibenzyltin dichloride was synthesized by the direct reaction of benzyl chloride (Merck) and metallic tin powder (Merck) in toluene according to a literature procedure [6]. The hydrazone ligand was prepared by the condensation of salicylaldehyde (Sigma Aldrich, 0.55 mL, 5.0 mmol) and 4-chlorobenzhydrazide (Sigma Aldrich, 0.86 g, 5.0 mmol) in hot methanol (25 mL). Dibenzyltin dichloride (0.37 g, 1 mmol) and the ligand (0.28 g, 1.0 mmol) were dissolved in methanol (30 mL). The mixture was refluxed for 2 h and filtered. The filtrate was allowed to stand at room temperature where upon yellow crystals were obtained from slow evaporation. The product was filtered, washed with minimum amount of methanol and air-dried. Yield: 0.34 g (62.2%). *M*.pt: 495–497 K. Anal. Calc. for C$_{23}$H$_{19}$Cl$_2$N$_2$O$_3$Sn: C 49.09; H 3.38; N 4.98%. Found: C 49.12; H 3.75; N 5.25%. IR (cm^{-1}) 1610 (*s*) ν(C−N), 1542 (*s*) ν(C−O). ^{1}H NMR (DMSO-d_6, p.p.m.): δ 3.10 (s, 2H, CH$_2$), 3.47 (s, 3H, CH$_3$), 6.85 (d, 2H, $J = 7.7$ Hz, Ph−H), 7.15–7.38 (m, 5H, Ph−H), 7.42 (d, 2H, $J = 7.8$ Hz, Ph−H), 7.62 (d, 2H, $J = 8.0$ Hz, Ph−H), 8.04 (d, 2H, $J = 8.0$ Hz, Ph−H), 8.83 (s, 1H, N=CH); OH not observed.

Experimental details

The C-bound H atoms were geometrically placed (C−H = 0.93−0.97 Å) and refined as riding with $U_{iso}(H) = 1.2$–1.5$U_{eq}(C)$. The O-bound H-atom was located in a difference Fourier map but was refined with a distance restraint

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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	0.17317(3)	0.22903(2)	0.69021(2)	0.03421(8)
Cl1	0.43522(14)	0.26194(14)	0.64689(5)	0.0631(3)
Cl2	−0.26747(19)	0.82267(14)	0.50698(5)	0.0673(4)
O1	0.0522(4)	0.3573(3)	0.64287(12)	0.0422(7)
O2	0.2677(4)	0.1566(3)	0.75814(13)	0.0452(7)
O3	−0.0685(4)	0.2203(3)	0.73642(12)	0.0466(7)
H3O	−0.086(7)	0.165(4)	0.7584(18)	0.070*
N1	0.1300(4)	0.5084(3)	0.70246(13)	0.0348(7)
N2	0.2007(4)	0.4087(3)	0.72955(13)	0.0333(7)
C1	0.0588(5)	0.4722(4)	0.65833(16)	0.0332(8)
C2	−0.0223(5)	0.5623(4)	0.62262(16)	0.0346(8)
C3	−0.0024(6)	0.6888(4)	0.62771(17)	0.0407(9)
H3	0.0631	0.7200	0.6551	0.049*
C4	−0.0784(5)	0.7694(4)	0.59270(16)	0.0448(9)
H4	−0.0652	0.8545	0.5966	0.054*
C5	−0.1744(5)	0.7225(4)	0.55173(15)	0.0437(8)
C6	−0.1948(7)	0.5993(5)	0.5457(2)	0.0618(14)
H6	−0.2606	0.5693	0.5181	0.074*
C7	−0.1175(6)	0.5165(4)	0.5806(2)	0.0556(13)
H7	−0.1296	0.4316	0.5759	0.067*
C8	0.2941(5)	0.4313(4)	0.77008(16)	0.0359(9)
H8	0.3093	0.5139	0.7795	0.043*
C9	0.3766(5)	0.3397(4)	0.80190(17)	0.0362(9)
C10	0.3631(5)	0.2102(4)	0.79500(16)	0.0394(10)
C11	0.4515(6)	0.1316(5)	0.82922(19)	0.0476(11)
H11	0.4453	0.0462	0.8246	0.057*
C12	0.5475(6)	0.1796(6)	0.8696(2)	0.0552(13)
H12	0.6060	0.1260	0.8917	0.066*
C13	0.5586(6)	0.3054(5)	0.8780(2)	0.0549(13)
H13	0.6214	0.3364	0.9061	0.066*
C14	0.4758(6)	0.3843(5)	0.84428(18)	0.0459(10)
H14	0.4852	0.4693	0.8495	0.055*
C15	−0.2044(6)	0.3034(5)	0.7391(2)	0.0617(14)
H15A	−0.1655	0.3849	0.7479	0.093*
H15B	−0.2800	0.2758	0.7662	0.093*
H15C	−0.2593	0.3056	0.7051	0.093*
C16	0.0936(6)	0.0631(4)	0.64952(17)	0.0382(9)
H16A	0.1887	0.0125	0.6409	0.046*
H16B	0.0225	0.0155	0.6730	0.046*
C17	0.0025(6)	0.0943(4)	0.59894(19)	0.0441(10)
C18	0.0817(7)	0.1017(5)	0.5497(2)	0.0585(13)
H18	0.1952	0.0906	0.5482	0.070*
C19	−0.0033(9)	0.1249(5)	0.5034(2)	0.0644(14)
H19	0.0528	0.1283	0.4710	0.077*
C20	−0.1685(9)	0.1430(5)	0.5044(2)	0.0707(15)
H20	−0.2257	0.1587	0.4728	0.085*
C21	−0.2514(7)	0.1379(6)	0.5533(2)	0.0654(15)
H21	−0.3646	0.1505	0.5545	0.078*
C22	−0.1665(7)	0.1146(4)	0.5989(2)	0.0524(11)
H22	−0.2232	0.1122	0.6313	0.063*

O—H = 0.82 ± 0.01 Å, and with U_{iso}(H) set to 1.5U_{eq}(O). The absolute structure was determined based on differences in Friedel pairs [4].

Comment

The motivation of on-going investigations on organotin compounds featuring a tridentate hydrazone ligand related to that in the title compound arise as a result of their potential as chemotherapeutic agents [7–10], a well known attribute of organotin compounds [11]. In continuation of structural studies in this area [12–16], the title organotin hydrazone, (I), has been investigated by X-ray crystallography.

The molecular structure of the title compound (I) is shown in the figure (35% displacement ellipsoids) and features a tin atom coordinated by the dianionic, tridentate hydrazone ligand, *via* the oxide-O1, phenoxide-O2 and imine-N2 atoms, a chloride, a methylene-carbon atom of the benzyl substitutent and a methanol molecule. The resultant CClNO$_3$ coordination geometry is based on an octahedron. Deviations from the ideal 180° angle are observed O1—Sn—O2 [156.86(12)°], N2—Sn—C16 [168.16(15)°] and Cl1—Sn—O3 [172.98(10)°]. These deviations are related, to a large extent, to the acute bite angles subtended at the tin atom by the five- and six-membered chelate rings. Thus, O1—Sn—N2 is 73.24(11)° and O2—Sn—N2 is 85.81(12)°. The N,*O*,O donor atoms of the tridentate ligand occupy *mer*-positions in the octahedron. The Sn—O1(oxide) and Sn—O2(phenoxide) bond lengths of 2.069(3) and 2.020(3) Å are not greatly different and each is shorter, as expected, than the Sn—O3(methanol) bond length of 2.279(3) Å. The Sn—N2 bond length is 2.186(3) Å, while those of Sn—Cl1 and Sn—C16 are 2.4143(11) and 2.159(4) Å, respectively. There is considerable delocalization of π-electron density over the O1—C1—N1—N2—C8 chromophore as seen in the C1—O1 [1.300(5) Å], C1—N1 [1.305(5) Å], N1—N2 [1.395(4) Å] and C8—N2 [1.288(5) Å] bond lengths. As indicated above, the chelating mode of the tridentate hydrazone ligand leads to the formation of five- and six-membered rings. The r.m.s. deviation of the five fitted atoms of the five-membered chelate ring is 0.0128 Å with the maximum deviation being 0.018(2) Å for the O1 atom. By contrast to this planar chelate ring, the r.m.s. deviation of the six atoms comprising the six-membered chelate ring = 0.1048 Å, with the maximum deviation of 0.154(2) Å being for the O2 atom. Thus, the six-membered ring is best described as being an envelope with the O2 atom lying 0.288(4) Å out of the least-squares plane defined by the five remaining atoms [r.m.s. deviation = 0.0658 Å]. The chelate rings are approximately co-planar with the dihedral angle between these being 6.2(2)°. The dihedral angle between the five-membered ring and the appended phenyl ring is 11.7(2)°, and the dihedral angle between the six-membered chelate ring and attached phenyl ring is 5.7(2)°, indicating an effectively co-planar relationship. The benzyl substituent is folded to lie over the hydrazone residue and the dihedral angle between it and each of the best planes through the five- and six-membered chelate rings

are 78.24(14) and 84.39(15)°, respectively, again indicating an approximately orthogonal disposition in each case.

A very similar coordination geometry to that reported herein has been observed previously in the structure of chlorido-(4-chloro-N-[(4-methoxy-2-oxidophenyl) methylidene] benzenecarbohydrazonato)-(4-fluorobenzyl)-methanol-tin(IV) [10]. The title compound is the product in the attempt to synthesize complex molecules of the general formula di-(substituted-benzyl)tin(L^n), where H_2L^n is a substituted hydrazone molecule, from the reaction of di-(substituted-benzyl)tin dichloride with H_2L^n. While such species, *e.g.* (2-$FC_6H_4CH_2)_2Sn(L^1)$, where H_2L^1 is 4-chloro-N'-[(1E)-(5-chloro-2-hydroxyphenyl)methylidene] benzohydrazide, can be formed [16], other incomplete reaction products are also sometimes obtained, *e.g.* (4-$FC_6H_4CH_2)Sn(OH_2)(L^3)$Cl, where H_2L^3 is 1-hydroxy-N'-[(1E)-(2-hydroxy-4-methoxyphenyl)methylidene] naphthalene-2-carbohydrazide [15]. Clearly, the nature of the ultimate reaction product is highly dependent on the reaction conditions and reagents employed.

The key feature of the molecular packing is the formation of a helical supramolecular chain along the *b* axis direction mediated by methanol-O—$H\cdots N$(imine) hydrogen bonding [O3—H3o$\cdots$N1^i: H3o$\cdots$N1^i = 1.99(4) Å, O3$\cdots$N1^i = 2.795(5) Å with angle at H3o = 170(5)° for symmetry operation (i) $-x$, $-1/2+y$, $3/2-z$]. The chains are connected into a layer in the *ab*-plane by a combination of π—π stacking interactions between the two different phenyl moieties of the hydrazone ligand [Cg(C2—C7)$\cdots$$Cg$(C9—C14)^{ii} = 3.738(3) Å with angle of inclination = 1.6(2)° for (ii) $-x$, $1/2+y$, $3/2-z$] and C—H$\cdots$$\pi$(phenyl) [C15—H15$b\cdots$$Cg$(C9—C14)^{iii}: H15$b\cdots$$Cg$(C9—C14)^{iii} = 2.74 Å, C15$\cdots$$Cg$(C9—C14)^{iii} = 3.670(5) Å with angle at H15b = 164° for (iii) $-1+x$, y, z] interactions. The intermolecular links along the *c* axis to consolidate a three-dimensional architecture are end-on and side-on C—Cl$\cdots$$\pi$(phenyl) interactions involving the same hydrazone-bound chloride atom interacting with two different rings [C5—Cl2$\cdots$$Cg$(C2—C7)^{iv}: Cl2$\cdots$$Cg$(C2—C7)^{iv} = 3.585(2) Å, C5$\cdots$$Cg$(C2—C7)^{iv} 5.093(4) Å with angle at Cl2 = 144.56(16)° and C5—Cl2$\cdots$$Cg$(C17—C22)^v: Cl2$\cdots$$Cg$(C17—C22)^v = 3.703(3) Å, C5$\cdots$$Cg$(C17—C22)^v = 4.347(5) Å with angle at Cl2 = 99.88(15)° for (iv) $-1/2+x$, $3/2-y$, $1-z$ and (v) x, $1+y$, z].

An analysis of the molecular packing was conducted by calculating the Hirshfeld surface to determine the major percentage contributors to the surface. This was conducted with Crystal Explorer 17 [17] in accord with standard procedures [18]; accordingly, the Hirshfeld surfaces were calculated as were the full and delineated two-dimensional fingerprint plots. The greatest percentage contribution to the surface contacts come from H$\cdots$H [46.7%] with significant contributions, not unexpectedly, from Cl$\cdots$H/H$\cdots$Cl [17.7%] and C$\cdots$H/H$\cdots$C [16.5%] contacts, reflecting the discussion above. Other notable percentage contributors are Cl$\cdots$C/C$\cdots$Cl [6.2%], O$\cdots$H/H$\cdots$O [4.1%], C$\cdots$C [4.0%] and N$\cdots$H/H$\cdots$N [3.9%] contacts.

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