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Crystal structure of (4-chloro-*N*-[(2-oxido-5-chlorophenyl)methylidene]benzene-carbohydrazonato- $\kappa^3 N, O, O'$)bis(2-fluorobenzyl)tin(IV), $C_{28}H_{20}Cl_2F_2N_2O_2Sn$

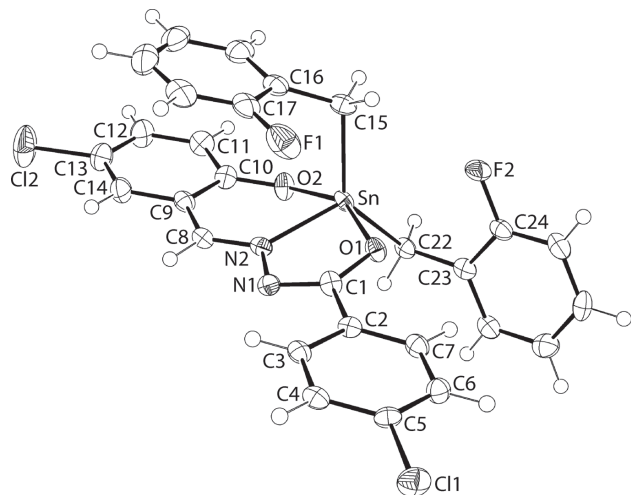


Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.10 × 0.06 × 0.05 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	10.4 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	31218, 4510, 0.044
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4309
$N(param)_{refined}$:	334
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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Abstract

$C_{28}H_{20}Cl_2F_2N_2O_2Sn$, monoclinic, $P2_1/c$ (no. 14), $a = 27.8125(4)$ Å, $b = 8.4443(2)$ Å, $c = 10.7891(1)$ Å, $\beta = 91.074(1)^\circ$, $V = 2533.45(7)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0600$, $wR_{ref}(F^2) = 0.1608$, $T = 100(2)$ K.

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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

All chemicals and solvents were used as purchased without purification. The melting point of the compound was measured on a Mel-Temp II digital melting point apparatus

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and was uncorrected. 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 ¹H NMR spectrum was recorded in DMSO-*d*₆ solution on a Jeol JNM-ECA 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

4-Chloro-*N'*-(5-chloro-2-hydroxybenzylidene)benzohydrazide was synthesized from 4-chlorobenzhydrazide (Sigma Aldrich) and 5-chlorosalicylaldehyde (Sigma Aldrich) in a 1:1 molar ratio. Di(2-fluorobenzyl)tin dichloride was synthesized by the direct reaction of 2-fluorobenzyl chloride (Merck) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. Di(2-fluorobenzyl)tin dichloride (0.41 g, 1 mmol) and 4-chloro-*N'*-(5-chloro-2-hydroxybenzylidene)benzohydrazide (0.32 g, 1 mmol) were dissolved in methanol (25 mL) and was refluxed for 3 h. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. The crystals were filtered, washed with a minimum amount of methanol and air-dried. Yield: 0.11 g (17%). **M.pt.**: 415–417 K. **IR** (cm⁻¹): 1648 (s) ν (C=O), 1605 (s) ν (C–N), 1605 (s) ν (C–N), 1078 (s) ν (C–O). **¹H NMR** (DMSO-*d*₆, ppm): δ 3.03 (s, 4H, CH₂), 7.01–7.26 (m, 8H, Ph-H), 7.41–7.50 (m, 4H, Ph-H), 7.70–7.98 (s, 3H, Ph-H), 8.75 (s, 1H, CH).

Experimental details

Hydrogen atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. Owing to poor agreement, a limited number of reflections, i.e. (7 1 1), (5 2 0), (3 1 1), (–7 1 1), (1 0 2) and

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Sn	0.74877(2)	0.33125(6)	0.51426(4)	0.01866(17)
Cl1	0.97627(7)	0.8938(3)	0.8801(2)	0.0320(5)
Cl2	0.50722(9)	0.4327(4)	0.7825(3)	0.0587(8)
F1	0.7371(2)	0.7436(8)	0.5071(5)	0.0480(15)
F2	0.82051(17)	0.2973(6)	0.3184(4)	0.0287(11)
O1	0.81024(19)	0.4689(7)	0.5681(5)	0.0219(12)
O2	0.6838(2)	0.2135(7)	0.5486(5)	0.0269(13)
N1	0.7668(2)	0.5466(8)	0.7391(6)	0.0205(14)
N2	0.7312(2)	0.4549(8)	0.6841(6)	0.0204(14)
C1	0.8059(3)	0.5442(10)	0.6716(7)	0.0211(16)
C2	0.8480(3)	0.6326(9)	0.7211(7)	0.0181(15)
C3	0.8417(3)	0.7496(9)	0.8105(7)	0.0201(16)
H3	0.8103	0.7727	0.8385	0.024*
C4	0.8808(3)	0.8329(9)	0.8591(7)	0.0210(16)
H4	0.8766	0.9135	0.9194	0.025*
C5	0.9264(3)	0.7946(9)	0.8168(7)	0.0201(16)
C6	0.9336(3)	0.6814(10)	0.7279(7)	0.0237(17)
H6	0.9649	0.6593	0.6991	0.028*
C7	0.8937(3)	0.5996(10)	0.6809(7)	0.0223(17)
H7	0.8981	0.5197	0.6202	0.027*
C8	0.6890(3)	0.4676(10)	0.7344(7)	0.0220(17)
H8	0.6867	0.5347	0.8047	0.026*
C9	0.6459(3)	0.3890(10)	0.6928(7)	0.0219(17)
C10	0.6449(3)	0.2686(10)	0.6010(8)	0.0245(17)
C11	0.5997(3)	0.2054(11)	0.5663(8)	0.0290(19)
H11	0.5982	0.1260	0.5039	0.035*
C12	0.5576(3)	0.2549(12)	0.6199(9)	0.033(2)
H12	0.5276	0.2095	0.5956	0.039*
C13	0.5599(3)	0.3739(12)	0.7113(9)	0.033(2)
C14	0.6026(3)	0.4388(11)	0.7461(8)	0.0286(19)
H14	0.6034	0.5193	0.8076	0.034*
C15	0.7213(3)	0.4776(10)	0.3651(7)	0.0243(17)
H15A	0.7473	0.5455	0.3334	0.029*
H15B	0.7093	0.4099	0.2963	0.029*
C16	0.6809(3)	0.5798(10)	0.4116(7)	0.0251(18)
C17	0.6908(3)	0.7107(11)	0.4854(8)	0.031(2)
C18	0.6563(4)	0.8018(11)	0.5378(9)	0.036(2)
H18	0.6648	0.8912	0.5869	0.044*
C19	0.6082(4)	0.7614(13)	0.5180(10)	0.044(3)
H19	0.5835	0.8212	0.5556	0.053*
C20	0.5967(4)	0.6331(13)	0.4428(10)	0.042(2)
H20	0.5640	0.6064	0.4274	0.050*
C21	0.6332(3)	0.5423(12)	0.3893(9)	0.034(2)
H21	0.6251	0.4549	0.3377	0.041*
C22	0.7871(3)	0.1116(9)	0.5143(7)	0.0210(16)
H22A	0.7841	0.0614	0.5967	0.025*
H22B	0.7718	0.0401	0.4524	0.025*
C23	0.8397(3)	0.1280(9)	0.4854(7)	0.0206(16)
C24	0.8552(3)	0.2190(10)	0.3868(7)	0.0231(17)
C25	0.9023(3)	0.2382(11)	0.3561(8)	0.0278(18)
H25	0.9110	0.3048	0.2891	0.033*
C26	0.9369(3)	0.1589(11)	0.4244(8)	0.0296(19)
H26	0.9698	0.1669	0.4032	0.035*
C27	0.9235(3)	0.0675(11)	0.5240(8)	0.031(2)
H27	0.9475	0.0157	0.5729	0.038*
C28	0.8755(3)	0.0500(10)	0.5537(7)	0.0245(17)
H28	0.8669	-0.0158	0.6213	0.029*

(7 0 2), were omitted from the final cycles of refinement. The maximum and minimum residual electron density peaks of 1.94 and 2.34 eÅ⁻³, respectively, were located 0.20 and 0.80 Å from the H21 and Sn atoms, respectively.

Comment

Recent crystal structure determinations of benzyltin compounds containing Schiff base ligands related to that in the title molecule, (2-FC₆H₄CH₂)₂Sn(L¹), where H₂L¹ is 4-chloro-*N'*-[(1*E*)-(5-chloro-2-hydroxyphenyl)methylidene] benzohydrazide, hereafter (I), have revealed the reaction of the precursor di-(substituted-benzyl)tin dichloride with 4-chloro-*N'*-[(1*E*)-(2-hydroxyphenyl)methylidene] benzohydrazide (H₂L²), gave (C₆H₅CH₂)Sn(OHCH₃)(L²)Cl [6], and with 1-hydroxy-*N'*-[(1*E*)-(2-hydroxy-4-methoxyphenyl)methylidene]naphthalene-2-carbohydrazide (H₂L³), yielded (4-FC₆H₄CH₂)Sn(OH₂)(L³)Cl [7], that is, X-ray crystallography indicated incomplete reaction products. The present crystal and molecular structure determination of (I) is of the anticipated product and full details are described herein.

The molecular structure of (I) is shown in the figure (50% displacement ellipsoids). The tin atom is bound by two methylene-carbon atoms of the benzyl substituents as well as the oxide-O1, phenoxide-O2 and imine-N2 donor atoms derived from the di-negative, tridentate hydrazone ligand. The Sn—O1(oxide) [2.139(5) Å] and Sn—O2(phenoxide) [2.101(5) Å] bond lengths are distinct and shorter than the Sn—N2 bond length [2.173(6) Å]. There is evidence of considerable delocalisation of π-electron density over the O1—C1—N1—N2—C8 chromophore as seen in the sequence of C1—O1 [1.293(10) Å], C1—N1 [1.321(10) Å], N1—N2 [1.383(9) Å] and C8—N2 [1.306(10) Å] bond lengths. The resultant C₂N₂O₂ donor set defines a highly distorted coordination geometry as suggested by the O1—Sn—O2 [153.5(2)°] and C15—Sn—C22 [131.8(3)°] bond angles. The tridentate mode of coordination of the Schiff base di-anion gives rise to five- and six-membered chelate rings. The angles subtended by these are acute, i.e. O1—Sn—N2 = 72.6(2)° and O2—Sn—N2 = 82.6(2)°, and contribute to the distortion of the coordination geometry. Five-coordinate geometries may be quantified by the value of τ, which is 0.0 for an ideal square-pyramidal coordination geometry and 1.0 for an ideal trigonal-bipyramidal geometry [8]. In the present case, the value of τ computes to 0.36 indicating a highly distorted geometry with a tendency towards square-pyramidal. As indicated above, there are five- and six-membered chelate rings in the molecule. The former is strictly planar with a r.m.s. deviation of 0.0176 Å for the fitted atoms. By contrast, the six-membered is non-planar and is best described as an envelope with with flap atom, Sn, lying 0.58(1) Å above the plane defined by the remaining five atoms [r.m.s. deviation = 0.0477 Å]. The dihedral angle between the

best planes through the chelate rings is $8.9(5)^\circ$ and the dihedral angle between the peripheral phenyl rings of $9.7(5)^\circ$ suggest that, to a first approximation, the Schiff base dianion is planar. One of the benzyl-phenyl rings (C16–C21) is folded over the Schiff base di-anion whereas the other (C23–C28) is orientated away from the molecule with the dihedral angle between it and the five-membered ring being $73.73(18)^\circ$, indicative of an orthogonal relationship. The aforementioned (C16–C21) ring is orientated to lie over the fused-ring system (C9–C14) with an inter-centroid distance of $3.809(5)$ Å and angle of inclination of $9.6(4)^\circ$.

In the absence of conventional hydrogen bonding interactions, the molecular packing in the crystal of (I) is sustained by weak non-covalent interactions. Thus, methylene-C–H \cdots N(imine) interactions [C22–H22b \cdots N1ⁱ: H22b \cdots N1ⁱ = 2.42 Å, C22 \cdots N1ⁱ = $3.295(10)$ Å with angle at H22b = 147° for symmetry operation (i) $x, 1/2 - y, -1/2 + z$] lead to a supramolecular zig-zag chain along the *c*-axis direction. The chains are linked into a supramolecular layer in the *bc*-plane by a combination of $\pi\cdots\pi$ interactions, between chlorophenyl and benzyl rings [inter-centroid Cg(C2–C7) \cdots Cg(C23–C28)ⁱⁱ distance = $3.632(5)$ Å and angle of inclination = $8.9(4)^\circ$ for (ii) $x, 1 + y, z$], benzyl-phenyl-C–H \cdots π (chlorophenyl) [C28–H28 \cdots Cg(C2–C7)ⁱⁱⁱ: H28 \cdots Cg(C2–C7)ⁱⁱⁱ = 2.83 Å, C28 \cdots Cg(C2–C7)ⁱⁱⁱ = $3.673(9)$ Å with angle at H28 = 148° for (iii) $x, -1 + y, z$] and parallel benzyl-F \cdots π (chelate ring) interactions [C24–F2 \cdots Cg(Sn,O1,N1,N2,C1)ⁱ = $3.262(5)$ Å with angle at F2 = $105.6(4)^\circ$]. The ability of chelate rings to participate in such interactions, analogous to organic π -systems, is increasingly being recognised as important in supramolecular chemistry [9]. The chloro substituents lie to either side of each layer; layers stack along the *a*-axis direction. The closest interactions in the inter-layer regions are Cl \cdots Cl [C5–Cl1 \cdots Cl1ⁱⁱⁱ = $3.395(3)$ Å with angle at Cl1 = $147.7(3)$ for (iii) $2 - x, 2 - y, 2 - z$] halogen bonding [10] on one side of the layer and weak fused-ring-C–H \cdots Cl(chlorophenyl) interactions on the other side of the layer [C13–Cl2 \cdots H12^{iv}: Cl2 \cdots H12^{iv} = 2.86 Å, C13 \cdots H12^{iv} = $3.44(1)$ Å with angle at Cl2 = 120° for (iv) $1 - x, -1/2 + y, 3/2 - z$].

A further analysis of the molecular packing was conducted by calculating the percentage contributions of the different contacts to the Hirshfeld surfaces as well as the overall and delineated two-dimensional fingerprint plots. This was achieved using Crystal Explorer 17 [11] and standard procedures [12]. Over 75% of contacts to the Hirshfeld surface

are contributed by H \cdots H [35.7%], C \cdots H/H \cdots C [20.4%] and Cl \cdots H/H \cdots Cl [19.7%] contacts. Significant contacts are also due to C \cdots C [4.6%], O \cdots H/H \cdots O [4.6%], N \cdots H/H \cdots N [2.8%] and Cl \cdots Cl [1.2%] contacts; the remaining contacts make less than 1% contributions.

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