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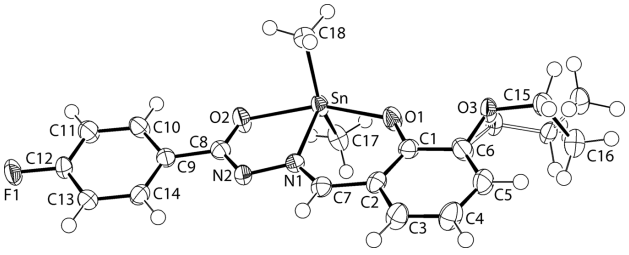
Crystal structure of {N-(3-ethoxy-2-oxidobenzylidene)-4-fluorobenzohydrazonato-κ³*O*,*N*,*O*′}dimethyltin(IV), $C_{18}H_{19}FN_2O_3Sn$



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Abstract

$C_{18}H_{19}FN_2O_3Sn$, monoclinic, *C*2/*c* (no. 15), $a = 27.1120(3)$ Å, $b = 9.5721(1)$ Å, $c = 13.3072(1)$ Å, $\beta = 98.271(1)°$, $V = 3417.55(6)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.016$, $wR_{ref}(F^2) = 0.043$, $T = 100(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

The *N*-(3-ethoxy-2-hydroxybenzylidene)-4-fluorobenzohydrazonic acid was prepared from the 1:1 molar reaction of 4-fluorobenzoic hydrazide (Aldrich; 0.15 g, 1 mmol) with 3-ethoxysalicylaldehyde (Aldrich; 0.17 g, 1 mmol) in methanol (25 mL) solution. The obtained acid was purified and used in the preparation of the title compound. Triethylamine (Merck; 0.14 mL, 1 mmol) was added to a methanol solution (5 mL) of the acid prepared above (0.30 g, 1 mmol) and stirred. After 0.5 h, dimethyltin dichloride (TCI; 0.22 g, 1 mmol) was added to the mixture. The mixture was refluxed for 3 h. Yellow precipitates were obtained upon slow evaporation. The precipitate was washed with hexane and recrystallized from ethanol solution. Yellow crystals were obtained from the slow evaporation of this solution. **Yield**: 62%; **M.p.**: 438–439 K. **IR** (ATR, cm^{-1}): 1650, 1606, 1573 (s, C=N–N=C), 590 (w, Sn–O), 461 (w, Sn–N). **^{1}H NMR** (in $CDCl_3$): 0.83 (s, 6H, Sn–CH_3), 1.45–1.52 (m, 3H, –OCH_2CH_3), 4.16–4.27 (m, 2H, –OCH_2CH_3), 6.62–6.72 (m, 1H, aromatic H), 6.82–7.16 (m, 4H, aromatic H), 8.06–8.20 (m, 2H, aromatic H), 8.68 (s, 1H, HC=N).

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.14 × 0.11 × 0.08 mm
Wavelength:	Cu *Kα* radiation (1.54178 Å)
μ:	121.7 cm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, Dualflex, AtlasS2, ω scans
$2\theta_{max}$, completeness:	134.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	19108, 3054, 0.021
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2973
$N(param)_{refined}$:	257
Programs:	Oxford programs [1], SHELX [2, 3], ORTEP [4]

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$. The ethoxy group was found to be disordered over two positions. Refinement revealed the major component had a site occupancy factor = 0.505(8). Thus the occupancies of the disordered atoms were fixed at 0.5.

Discussion

Metal complexes of the hydrazone ligand [5], including those of organotin [6, 7], are known to exhibit encouraging anti-microbial and anti-tumour potential. In continuation of related structural studies, the title compound has been structurally characterised and compared with its diphenyltin analogue [8].

The title structure is shown in the figure (70% displacement ellipsoids; one component of the disordered ethoxy

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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	1.03593(2)	0.18572(2)	0.54436(2)	0.01938(5)
F1	1.23392(4)	0.83093(11)	0.76403(10)	0.0307(3)
O1	0.95968(4)	0.11587(13)	0.52846(10)	0.0259(3)
O2	1.09603(5)	0.33896(13)	0.57464(10)	0.0246(3)
O3[a]	0.87769(16)	−0.0365(5)	0.5139(3)	0.0206(8)
O3′[a]	0.87368(17)	−0.0243(5)	0.4702(3)	0.0195(8)
N1	1.00493(5)	0.37540(15)	0.60330(10)	0.0174(3)
N2	1.03850(5)	0.48275(15)	0.63577(11)	0.0184(3)
C1	0.91867(7)	0.17438(18)	0.55216(14)	0.0192(4)
C2	0.91703(7)	0.30860(18)	0.59516(13)	0.0183(4)
C3	0.87167(7)	0.3645(2)	0.61810(14)	0.0249(4)
H3	0.8713	0.4552	0.6470	0.030*
C4	0.82829(7)	0.2899(2)	0.59934(15)	0.0270(4)
H4	0.7980	0.3282	0.6153	0.032*
C5	0.82902(7)	0.1569(2)	0.55643(15)	0.0254(4)
H5	0.7989	0.1052	0.5427	0.030*
C6	0.87269(7)	0.0997(2)	0.53373(15)	0.0253(4)
C7	0.95958(6)	0.39878(19)	0.61917(12)	0.0184(3)
H7	0.9538	0.4854	0.6502	0.022*
C8	1.08356(7)	0.45227(18)	0.61761(12)	0.0181(3)
C9	1.12316(6)	0.55560(18)	0.65236(12)	0.0174(3)
C10	1.17296(7)	0.52091(19)	0.65213(14)	0.0223(4)
H10	1.1813	0.4331	0.6258	0.027*
C11	1.21060(7)	0.6129(2)	0.68982(15)	0.0251(4)
H11	1.2447	0.5891	0.6904	0.030*
C12	1.19717(7)	0.73946(19)	0.72642(14)	0.0214(4)
C13	1.14843(7)	0.77872(19)	0.72732(14)	0.0213(4)
H13	1.1405	0.8671	0.7533	0.026*
C14	1.11134(7)	0.68607(18)	0.68941(14)	0.0204(4)
H14	1.0774	0.7113	0.6885	0.025*
C15[a]	0.83344(14)	−0.1226(4)	0.5047(3)	0.0213(8)
H15A[a]	0.8140	−0.0991	0.5599	0.026*
H15B[a]	0.8433	−0.2221	0.5122	0.026*
C16[a]	0.80136(19)	−0.1014(5)	0.4034(3)	0.0278(10)
H16A	0.7717	−0.1608	0.3994	0.042*
H16B[a]	0.8204	−0.1265	0.3487	0.042*
H16C[a]	0.7912	−0.0033	0.3962	0.042*
C15′[a]	0.82725(16)	−0.0866(4)	0.4251(3)	0.0191(8)
H15C[a]	0.8332	−0.1421	0.3652	0.023*
H15D[a]	0.8034	−0.0113	0.4010	0.023*
C16′[a]	0.80407(16)	−0.1798(4)	0.4971(3)	0.0242(8)
H16D[a]	0.7729	−0.2192	0.4619	0.036*
H16E[a]	0.7971	−0.1250	0.5556	0.036*
H16F[a]	0.8272	−0.2557	0.5204	0.036*
C17	1.03680(8)	0.2026(2)	0.38741(15)	0.0264(4)
H17A	1.0291	0.1115	0.3553	0.040*

[a]Occupancy: 0.5.

group is shown with open bonds). The tin(IV) centre is five-coordinate within a C_2NO_2 donor set derived from N,O,O atoms of the dinegative, tridentate ligand and two methyl-C atoms.

Compared to the ideal τ values of 0.0 for an ideal square-pyramid and 1.0 for an ideal trigonal-bipyramid [9], the value of $\tau = 0.13$ is indicative of a square-pyramidal geometry. In this description, the O1, O2, C17 and C18 atoms define the basal plane and the N1 atom occupies the apical position. The r.m.s. deviations of the four atoms defining the basal plane is 0.53 Å and their deviations are great at 0.5172(9), 0.5424(10), −0.5418(10) and −0.5179(10) Å, respectively. The tin atom lies 0.0598(8) Å out of the plane in the direction of the N1 atom. As expected, the widest angles subtended at the tin atom are in the basal plane, i.e. O1–Sn–O2 of 154.91(5)° and C17–Sn–C18 of 147.23(8)°.

As a result of the N,O,O coordination mode of the Schiff base dianion, both five- and six-membered chelate rings are formed. Both rings are planar with r.m.s. deviations of 0.0327 Å for the Sn,O2,N1,N2,C8 chelate ring and 0.0160 Å for the Sn,O1,N1,C1,C2,C7 chelate. The rings form a dihedral angle of 1.97(5)°. Indeed, the $C_7N_2O_2Sn$ atoms of all but the 4-fluorophenyl ring of the Schiff base ligand are coplanar, exhibiting a r.m.s. deviation of 0.0272 Å; the 4-fluorophenyl ring is slightly twisted out of this plane, forming a dihedral angle of 9.30(6)°.

The most closely related structure available for comparison is the recently described diphenyl analogue [8]. Here, the coordination geometry is almost exactly intermediate between the ideal extremes with $\tau = 0.43$. The difference between the structures is readily rationalised in terms of steric effects. With smaller tin-bound methyl groups, centrosymmetrically related molecules in the title crystal can approach each other *via* secondary Sn···O bonding interactions [10] to form a dinuclear aggregate. Thus, the Sn···O1^1, O3^i and O3′^{i} separations are 3.0529(13), 2.941(4) and 2.927(5) Å, respectively, for symmetry operation i: $2-x, -y, 1-z$. No such interactions are apparent in the diphenyltin analogue owing to steric congestion.

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