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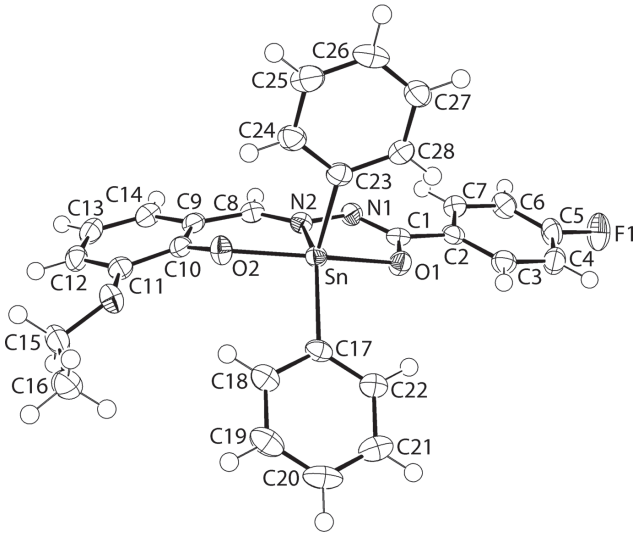
Crystal structure of (*N*-(3-ethoxy-2-oxidobenzylidene)-4-fluorobenzohydrazonato-κ³*N*,*O*,*O*′)-diphenyltin(IV), $C_{28}H_{23}FN_2O_3Sn$



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Abstract

$C_{28}H_{23}FN_2O_3Sn$, orthorhombic, *Pbca* (no. 61), $a = 16.0887(2)$ Å, $b = 14.5333(2)$ Å, $c = 20.5550(2)$ Å, $V = 4806.21(10)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0199$, $wR_{ref}(F^2) = 0.0596$, $T = 100(2)$ K.

CCDC no.: 1818060

Source of materials

N-(3-ethoxy-2-hydroxybenzylidene)-4-fluorobenzohydrazonic acid ($ligH_2$) was prepared from a 1:1 reaction of 4-fluorobenzoic hydrazide (Aldrich; 0.15 g, 1 mmol) with 3-ethoxysalicylaldehyde (Aldrich; 0.17 g, 1 mmol) in methanol solution (25 mL). The obtained product ($ligH_2$) was purified and used in the preparation of the title compound. Triethylamine (Merck; 0.14 ml, 1 mmol) was added to a methanol

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Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.16 × 0.11 × 0.09 mm
Wavelength:	Cu *Kα* radiation (1.54178 Å)
μ:	88.0 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}:	27905, 4285, 0.023
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3927
$N(param)_{refined}$:	316
Programs:	Oxford programs [1], SHELX [2, 3], ORTEP [4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn	0.00136(2)	0.78741(2)	0.61417(2)	0.01468(6)
F1	−0.10797(8)	1.05010(8)	0.96567(5)	0.0346(3)
O1	−0.00429(6)	0.84531(9)	0.70902(6)	0.0185(3)
O2	−0.00896(7)	0.78848(8)	0.51432(7)	0.0202(3)
O3	0.05764(8)	0.78553(8)	0.39876(6)	0.0218(3)
N1	−0.10555(8)	0.94312(10)	0.66778(6)	0.0181(3)
N2	−0.08170(8)	0.90464(10)	0.60825(6)	0.0169(3)
C1	−0.06118(9)	0.90886(11)	0.71554(8)	0.0164(3)
C2	−0.07494(10)	0.94642(11)	0.78169(8)	0.0174(3)
C3	−0.02471(11)	0.91687(12)	0.83284(9)	0.0209(4)
H3	0.0176	0.8726	0.8249	0.025*
C4	−0.03562(12)	0.95119(13)	0.89522(8)	0.0238(4)
H4	−0.0014	0.9312	0.9302	0.029*
C5	−0.09747(11)	1.01510(13)	0.90490(8)	0.0239(4)
C6	−0.14895(11)	1.04607(12)	0.85589(8)	0.0230(4)
H6	−0.1914	1.0899	0.8645	0.028*
C7	−0.13710(10)	1.01152(12)	0.79378(8)	0.0195(3)
H7	−0.1714	1.0322	0.7591	0.023*
C8	−0.11039(10)	0.94581(12)	0.55679(8)	0.0176(3)
H8	−0.1492	0.9941	0.5636	0.021*
C9	−0.08882(10)	0.92496(12)	0.49055(8)	0.0176(3)
C10	−0.03344(10)	0.85347(11)	0.47364(8)	0.0170(3)
C11	−0.00255(9)	0.85051(13)	0.40892(10)	0.0185(4)
C12	−0.03379(11)	0.90918(12)	0.36209(8)	0.0214(4)
H12	−0.0149	0.9044	0.3184	0.026*
C13	−0.09317(11)	0.97568(13)	0.37852(8)	0.0222(4)
H13	−0.1156	1.0145	0.3457	0.027*
C14	−0.11914(10)	0.98492(12)	0.44175(8)	0.0207(4)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H14	−0.1577	1.0319	0.4529	0.025*
C15	0.10990(12)	0.79717(12)	0.34254(8)	0.0240(4)
H15A	0.1270	0.8623	0.3381	0.029*
H15B	0.0798	0.7787	0.3026	0.029*
C16	0.18475(12)	0.73677(15)	0.35270(10)	0.0294(4)
H16A	0.2222	0.7426	0.3154	0.044*
H16B	0.2139	0.7558	0.3924	0.044*
H16C	0.1669	0.6726	0.3570	0.044*
C17	0.13310(11)	0.78392(11)	0.61258(8)	0.0176(4)
C18	0.17405(11)	0.76355(12)	0.55452(9)	0.0215(4)
H18	0.1432	0.7536	0.5157	0.026*
C19	0.26051(11)	0.75790(13)	0.55378(9)	0.0274(4)
H19	0.2886	0.7443	0.5143	0.033*
C20	0.30580(12)	0.77200(14)	0.61030(10)	0.0292(5)
H20	0.3647	0.7680	0.6095	0.035*
C21	0.26516(11)	0.79186(12)	0.66787(10)	0.0266(4)
H21	0.2963	0.8016	0.7065	0.032*
C22	0.17882(11)	0.79759(12)	0.66933(9)	0.0210(4)
H22	0.1511	0.8108	0.7090	0.025*
C23	−0.07937(10)	0.67531(12)	0.63303(8)	0.0177(3)
C24	−0.11279(10)	0.62365(12)	0.58194(9)	0.0219(4)
H24	−0.0967	0.6362	0.5384	0.026*
C25	−0.16950(11)	0.55411(13)	0.59494(10)	0.0268(4)
H25	−0.1921	0.5192	0.5601	0.032*
C26	−0.19344(11)	0.53516(13)	0.65825(9)	0.0263(4)
H26	−0.2325	0.4876	0.6668	0.032*
C27	−0.16021(11)	0.58571(13)	0.70910(9)	0.0253(4)
H27	−0.1762	0.5725	0.7526	0.030*
C28	−0.10349(10)	0.65581(12)	0.69661(8)	0.0217(4)
H28	−0.0811	0.6905	0.7316	0.026*

solution (5 mL) of $ligH_2$ (0.30 g, 1 mmol) and stirred. After 0.5 h, diphenyltin dichloride (Aldrich; 0.34 g, 1 mmol) was added. The mixture was refluxed for 3.5 h. Yellow precipitates were obtained upon slow evaporation. The precipitate was washed with hexane and recrystallised from ethanol solution. Yellow crystals were obtained from the slow evaporation of this solution. Yield: 55%; M.p.: 455–457 K. **IR** (ATR, cm^{-1}): 1648, 1610, 1605 (s, C=N—N=C), 596 (w, Sn–O), 477 (w, Sn–N). **^{1}H NMR** (in $CDCl_3$): 1.45–1.55 (m, 3H, $-OCH_2CH_3$), 4.15–4.40 (m, 2H, $-OCH_2CH_3$), 6.72–6.78 (m, 1H, aromatic H), 6.95–7.22 (m, 4H, aromatic H), 7.32–7.52 (m, 6H, aromatic H), 7.82–7.95 (m, 4H, aromatic H), 8.05–8.20 (m, 2H, aromatic H), 8.70 (s, 1H, HC=N).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$.

Comment

In bioinorganic chemistry, many hydrazones and their complexes have been tested and found to show promising biological applications especially in terms of anti-microbial and anti-tumour activities [5]. Organotin(IV) hydrazones have attracted interest in this context [6, 7]. The current structural report on the title compound is part of an on-going study focused upon the preparation of fluorinated organotin hydrazones, motivated by the increasing number of fluorinated anti-tumour agents in the market [8].

As shown in the figure (70% displacement ellipsoids), the tin(IV) centre is coordinated by the N,O,O atoms derived from the dianionic, tridentate Schiff base ligand and two ipso-C atoms derived from the tin-bound phenyl groups. The resulting C_2NO_2 donor set defines a highly distorted coordination geometry. This is seen in the value of $\tau = 0.4$, which compares to $\tau = 0.0$ for an ideal square-pyramid and 1.0 for an ideal trigonal-bipyramid [9]. The widest angle at the tin atom is subtended by the phenoxide-O atoms, *i.e.* O1—Sn—O2 = 155.21(5)°. The mode of coordination of the Schiff base ligand leads to the formation of five- and six-membered rings. The Sn,O1,N1,N2,C1 chelate ring is best described as having an envelope conformation with the Sn atom being the flap atom, lying 0.309(3) Å out of the plane defined by the remaining four atoms [r.m.s. deviation = 0.0068 Å]. While not as pronounced as for the aforementioned ring, the six-membered ring, comprising the Sn,O2,N2,C8—C10 atoms, is also based on an envelope, with the phenoxide-O2 atom being the flap atom, lying 0.2362(17) Å out of the plane defined by the remaining five atoms [r.m.s. deviation = 0.0136 Å]. The least-squares planes through the chelate rings are inclined to each other by an angle of 12.95(6)°. Indeed, the Schiff base ligand is curved with the dihedral angle between the outer phenyl rings being 24.45(8)°. The Sn-bound phenyl rings are orientated away from the Schiff base ligand and form a dihedral angle of 52.09(5)°; the C17—Sn—C23 angle is 126.65(6)°.

The identical Schiff base ligand to that reported herein has only just recently been structurally characterised, such as in vanadyl complexes whereby a similar tridentate N,O,O mode of coordination is found [10]. The most closely related organotin compound is one, where the fluoro substituent is replaced by a chloro substituent, and the ethoxy group is replaced by a methoxy moiety [11].

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