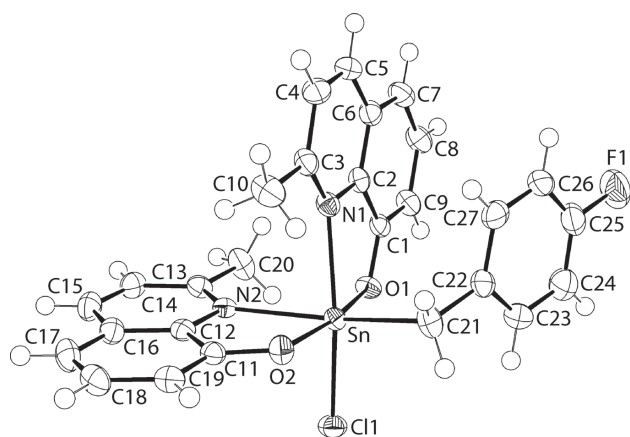


See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink\*

# Crystal structure of chlorido-4-fluorobenzyl-bis(2-methylquinolin-8-olato- $\kappa^2 N, O$ )tin(IV), $C_{27}H_{22}ClFN_2O_2Sn$



**Table 1:** Data collection and handling.

Crystal:	Colourless prism
Size:	0.23 × 0.12 × 0.07 mm
Wavelength:	Mo K $\alpha$ radiation (0.71073 Å)
$\mu$ :	1.26 mm <sup>-1</sup>
Diffractometer, scan mode:	CCD, $\varphi$ and $\omega$
$\theta_{\max}$ , completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	23534, 5789, 0.015
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$ , 5771
$N(\text{param})_{\text{refined}}$ :	310
Programs:	Bruker [1], SHELX [2–4], WinGX/ORTEP [5]

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## Abstract

$C_{27}H_{22}ClFN_2O_2Sn$ , tetragonal,  $P4_1$  (no. 76),  $a = 9.38970(10)$  Å,  $c = 26.2753(4)$  Å,  $V = 2316.60(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{\text{gt}}(F) = 0.0141$ ,  $wR_{\text{ref}}(F^2) = 0.0381$ ,  $T = 293(2)$  K.

CCDC no.: 1903610

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

**Instrumentation:** The elemental analysis was performed on a Perkin-Elmer EA2400 CHN analyser. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrophotometer in a Nujol mull between KBr plates. The

$^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded in  $\text{CDCl}_3$  solution on a Bruker AVN FT-NMR spectrometer with chemical shifts relative to  $\text{Me}_4\text{Si}$  for  $^1\text{H}$  and  $\text{CDCl}_3$  for  $^{13}\text{C}\{^1\text{H}\}$ .

**Synthesis:** Di(4-fluorobenzyl)tin dichloride was prepared from the direct synthesis method using tin powder (Sigma-Aldrich) and 4-fluorobenzyl chloride (Sigma-Aldrich) in toluene [6]. The ligand, 2-methyl-8-hydroxyquinoline (Sigma-Aldrich; 0.31 g, 2.0 mmol) and di(4-fluorobenzyl)tin dichloride (0.41 g, 1.0 mmol) were heated in 95% ethanol (50 mL) for 1 h. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. Yield: 0.35 g (60%). **M. pt:** 479–481 K. Calcd for  $C_{27}H_{22}ClFN_2O_2Sn$ : C 55.91; H 3.79; N 4.83%. Found: C 55.57; H 3.18; N 5.25%. **IR** ( $\text{cm}^{-1}$ ) 407 (w)  $\nu(\text{Sn}-\text{N})$ , 528 (m)  $\nu(\text{Sn}-\text{O})$ , 1108 (s)  $\nu(\text{C}-\text{O})$ , 1578 (s)  $\nu(\text{C}=\text{N})$ .  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , ppm):  $\delta$  6.67–6.76 (m, 4H, Ph-H), 3.15 (s, 2H, Ph- $\text{CH}_2$ ), 7.01–8.79 (m, 10H, oxin-H), 2.51 (s, 6H, oxin- $\text{CH}_3$ ).  **$^{13}\text{C}\{^1\text{H}\}\text{NMR}$**  ( $\text{CDCl}_3$ , ppm):  $\delta$  24.3 ( $\text{CH}_3$ ), 37.4 ( $\text{CH}_2$ ), 138.9, 128.0, 127.4, 123.8 (C-Ph), 113.9, 121.0, 121.8, 129.5, 130.6, 139.8, 140.4, 143.4, 155.1 (C-oxin).

## Experimental details

The C-bound H atoms were geometrically placed ( $\text{C}-\text{H} = 0.93\text{--}0.97$  Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Owing to poor agreement, the (0 0  $\bar{4}$ ) reflection was omitted from the final cycles of refinement. The sample was refined as a two-component inversion twin with the minor component refining to 0.074(12).

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	U <sub>iso</sub> <sup>*</sup> /U <sub>eq</sub>
Sn	0.56825(2)	0.96184(2)	0.47956(2)	0.01355(4)
Cl1	0.66301(6)	1.19480(6)	0.49951(2)	0.02051(10)
F1	1.06407(19)	0.4888(2)	0.54974(9)	0.0420(5)
O1	0.63761(17)	0.90109(17)	0.54997(6)	0.0160(3)
O2	0.46540(18)	1.03242(17)	0.41571(6)	0.0179(3)
N1	0.4625(2)	0.74188(19)	0.49075(7)	0.0155(4)
N2	0.3471(2)	1.04282(19)	0.50961(7)	0.0138(3)
C1	0.6127(2)	0.7666(2)	0.56379(8)	0.0154(4)
C2	0.5194(2)	0.6808(2)	0.53362(8)	0.0151(4)
C3	0.3767(2)	0.6666(2)	0.46073(9)	0.0179(4)
C4	0.3426(2)	0.5237(2)	0.47276(9)	0.0204(5)
H4	0.282351	0.472160	0.451554	0.025*
C5	0.3977(3)	0.4611(2)	0.51535(9)	0.0201(4)
H5	0.374424	0.367330	0.523125	0.024*
C6	0.4900(2)	0.5383(2)	0.54762(8)	0.0174(4)
C7	0.5531(3)	0.4821(3)	0.59211(9)	0.0213(4)
H7	0.535054	0.388506	0.601761	0.026*
C8	0.6409(3)	0.5661(3)	0.62099(9)	0.0211(4)
H8	0.681801	0.528917	0.650364	0.025*
C9	0.6705(2)	0.7081(2)	0.60695(9)	0.0187(4)
H9	0.730156	0.762902	0.627295	0.022*
C10	0.3149(3)	0.7365(3)	0.41464(10)	0.0254(5)
H10A	0.248888	0.809084	0.424975	0.038*
H10B	0.266125	0.666720	0.394422	0.038*
H10C	0.389912	0.778744	0.394935	0.038*
C11	0.3386(2)	1.0940(2)	0.42062(8)	0.0155(4)
C12	0.2730(2)	1.0992(2)	0.46928(8)	0.0144(4)
C13	0.2888(2)	1.0428(2)	0.55587(8)	0.0169(4)
C14	0.1508(3)	1.0992(2)	0.56331(9)	0.0198(4)
H14	0.110356	1.096664	0.595605	0.024*
C15	0.0760(3)	1.1570(3)	0.52406(9)	0.0211(5)
H15	-0.014270	1.194544	0.529728	0.025*
C16	0.1354(2)	1.1601(2)	0.47481(10)	0.0182(4)
C17	0.0648(3)	1.2160(3)	0.43187(10)	0.0220(5)
H17	-0.025846	1.255017	0.435070	0.026*
C18	0.1310(3)	1.2123(3)	0.38522(9)	0.0217(5)
H18	0.084993	1.250209	0.356964	0.026*
C19	0.2674(2)	1.1520(2)	0.37952(9)	0.0184(4)
H19	0.310218	1.151239	0.347602	0.022*
C20	0.3667(3)	0.9809(3)	0.60017(9)	0.0240(5)
H20A	0.375404	0.879747	0.595775	0.036*
H20B	0.315053	1.000456	0.630902	0.036*
H20C	0.459907	1.022575	0.602307	0.036*
C21	0.7359(3)	0.8699(3)	0.43242(9)	0.0222(5)
H21A	0.693391	0.822077	0.403434	0.027*
H21B	0.796745	0.945363	0.419666	0.027*
C22	0.8239(3)	0.7655(2)	0.46209(9)	0.0206(4)
C23	0.9402(3)	0.8128(3)	0.49020(10)	0.0263(5)
H23	0.963630	0.909028	0.489296	0.032*
C24	1.0227(3)	0.7212(3)	0.51963(11)	0.0299(6)
H24	1.100615	0.754665	0.537936	0.036*
C25	0.9854(3)	0.5800(3)	0.52075(11)	0.0275(5)
C26	0.8714(3)	0.5277(3)	0.49365(11)	0.0278(5)
H26	0.848502	0.431416	0.495057	0.033*
C27	0.7910(3)	0.6204(3)	0.46419(10)	0.0246(5)
H27	0.714276	0.585487	0.445606	0.029*

**Comment**

The chelating ability of 8-hydroxyquinoline (oxine) and its derivatives has resulted in the formation of a large number of metal-oxine complexes [7]. These derivatives of 8-hydroxyquinoline and their metal complexes are known to exhibit various biological activities [7, 8]. In our efforts to synthesise biologically active diorganotin-oxine complexes, the reaction of dibenzyltin dichlorides with various 8-hydroxyquinoline derivatives were performed. In general, the reaction would be expected to form product of the type Bz<sub>2</sub>SnCl(ox) or Bz<sub>2</sub>Sn(ox)<sub>2</sub> [Bz = benzyl; ox = 8-hydroxyquinolinyl derivative] by replacing either one of both chloride atoms of the diorganotin precursor [9, 10]. In the present study, where a 2:1 reaction of 2-methyl-8-hydroxyquinoline and di(4-fluorobenzyl)tin dichloride was performed, it was found that a mono(4-fluorobenzyl)tin compound was obtained as the predominant product.

The molecular structure is shown in the figure (70% displacement ellipsoids) and reveals the tin atom to be bis-*N,O*-chelated by two 2-methyl-8-hydroxyquinolinato ligands, one chlorido ligand and the 4-Bz-C atom to result in a CCIN<sub>2</sub>O<sub>2</sub> donor set. The coordination geometry approximates an octahedron in which the oxygen atoms are mutually arranged in *trans* position [O1–Sn–O2 = 169.61(6)°] and the nitrogen atoms are *cis* to each other [N1–Sn–N2 = 82.33(6)°]. The narrowest angle subtended at the tin atom is the O2–Sn–N2 chelate angle [75.73(6)°] while the widest angle is the aforementioned O1–Sn–O2 angle. Being mutually *trans*, the Sn–O1 and Sn–O2 bond lengths are experimentally equivalent [2.0426(16) and 2.0462(17) Å, respectively] but, there are systematic variations in the Sn–N bond lengths. Thus, the Sn–N1 bond length [2.3105(19) Å] is shorter than the Sn–N2 bond [2.3480(18) Å] which correlates with the N2 atom being *trans* to the benzyl-C21 atom [Sn–C1 = 2.181(2) Å]. The five-membered chelate rings adopt distinct conformations. The O1-chelate ring is best described as being an envelope with the tin atom lying 0.304(4) Å above the plane defined by the four remaining atoms of the ring [r.m.s. deviation = 0.005 Å]. By contrast, the O2-chelate ring is planar with the r.m.s. deviation of the five fitted atoms being 0.023 Å; the maximum deviation from the least-squares plane is 0.032(1) Å for the O2 atom. The dihedral angle between the best planes through the chelate rings is 84.48(5)°, consistent with an orthogonal relationship. Finally, the benzyl-ring is approximately folded towards the O1-chelate ring as seen in the dihedral angle of 24.33(11)° between them; the separation between the ring centroids of the respective rings is 3.5973(14) Å.

In the crystal, a combination of weak non-covalent interactions assemble the molecules into a three-dimensional network architecture. Thus, oxinate-C–H···O(oxinate) [C18–H18···O1<sup>i</sup>: H18···O1<sup>i</sup> = 2.52 Å, C18···O1<sup>i</sup> = 3.415(3) Å

with angle at  $H18 = 163^\circ$  for symmetry operation  $i: -1 + y, 2 - x, -1/4 + z$ , benzyl-C—H $\cdots$ Cl [C26—H26 $\cdots$ Cl1<sup>ii</sup>: H26 $\cdots$ Cl1<sup>ii</sup> = 2.83 Å, C26 $\cdots$ Cl1<sup>ii</sup> = 3.691(3) Å, angle at H26 = 155° for  $ii: x, -1 + y, z$ ] and oxinate-C—H $\cdots$  $\pi$ (NC<sub>5</sub>-oxinate) [C5—H5 $\cdots$  $\pi$ (N2, C12—C16)<sup>ii</sup>: H5 $\cdots$  $\pi$ (N2,C12—C16)<sup>ii</sup> = 2.94 Å, C5 $\cdots$  $\pi$ (N2,C12—C16)<sup>ii</sup> = 3.812(2) Å with angle at H5 = 156°] are readily identified points of contact between molecules.

There are two other structures in the literature that resemble that described herein, i.e. with general formula  $RSn(\text{oxine})_2Cl$ . In each of the  $R = n\text{-Bu}$  [11] and  $R = \text{Bz}$  [12] structures, very similar coordination geometries are noted.

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