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

Crystal structure of chlorido-4-fluorobenzyl-bis(2-methylquinolin-8-olato-κ²N,O)tin(IV), C₂₇H₂₂ClFN₂O₂Sn

Abstract
C₂₇H₂₂ClFN₂O₂Sn, tetragonal, P4₁ (no. 76), a = 9.38970(10) Å, c = 26.2753(4) Å, V = 2316.60(6) Å³, Z = 4, Rgt(F) = 0.0141, wRref(F²) = 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 ¹H and ¹³C{¹H} NMR spectra were recorded in CDCl₃ solution on a Bruker AVN FT-NMR spectrometer with chemical shifts relative to Me₄Si for ¹H and CDCl₃ for ¹³C{¹H}.

Synthesis: Di(4-fluorobenzyl)tin dichloride was prepared from the direct synthesis method. Di(4-fluorobenzyl)tin dichloride (0.41 g, 1.0 mmol) and di(4-fluorobenzyl)tin dichloride (0.31 g, 2.0 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 C₂₇H₂₂ClFN₂O₂Sn: C 55.91; H 3.79; N 4.83%. Found: C 55.57; H 3.18; N 5.25%.

Experimental details
The C-bound H atoms were geometrically placed (C–H = 0.93 – 0.97 Å) and refined as riding with Uiso(C) = 1.2Ueq(C). Owing to poor agreement, the (0 0 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).

Table 1: Data collection and handling.

<table>
<thead>
<tr>
<th>Crystal:</th>
<th>Colourless prism</th>
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<tbody>
<tr>
<td>Size:</td>
<td>0.23 × 0.12 × 0.07 mm</td>
</tr>
<tr>
<td>Wavelength:</td>
<td>Mo Kα radiation (0.71073 Å)</td>
</tr>
<tr>
<td>µ:</td>
<td>1.26 mm⁻¹</td>
</tr>
<tr>
<td>Diffractometer, scan mode:</td>
<td>CCD, φ and ω</td>
</tr>
<tr>
<td>θmax, completeness:</td>
<td>28.4°, &gt;99%</td>
</tr>
<tr>
<td>N(hkl)measured, N(hkl)unique, Rint:</td>
<td>23534, 5789, 0.015</td>
</tr>
<tr>
<td>Criterion for Iobs, N(hkl)gt:</td>
<td>Iobs &gt; 2σ(Iobs), 5771</td>
</tr>
<tr>
<td>N(param)refined:</td>
<td>310</td>
</tr>
<tr>
<td>Programs:</td>
<td>Bruker [1], SHELX [2–4], WinGX/ORTEP [5]</td>
</tr>
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</table>

¹H and ¹³C{¹H} NMR spectra were recorded in CDCl₃ solution on a Bruker AVN FT-NMR spectrometer with chemical shifts relative to Me₄Si for ¹H and CDCl₃ for ¹³C{¹H}.

¹H NMR (CDCl₃, ppm): δ 6.67 – 6.76 (m, 4H, Ph-H), 3.15 (s, 2H, Ph-CH₂), 7.01–8.79 (m, 10H, oxin-H), 2.51 (s, 6H, oxin-CH₃), 13(¹H)CNMR (CDCl₃, ppm): δ 24.3 (CH₃), 37.4 (CH₂), 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).
Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso/*/Ueq</th>
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<tr>
<td>Sn</td>
<td>0.56825(2)</td>
<td>0.96184(2)</td>
<td>0.47956(2)</td>
<td>0.01355(4)</td>
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<tr>
<td>C11</td>
<td>0.66301(6)</td>
<td>1.19480(6)</td>
<td>0.49951(2)</td>
<td>0.02051(10)</td>
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<tr>
<td>F1</td>
<td>1.06407(19)</td>
<td>0.48882(2)</td>
<td>0.54974(9)</td>
<td>0.0420(5)</td>
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<tr>
<td>O1</td>
<td>0.63761(17)</td>
<td>0.90109(17)</td>
<td>0.54997(6)</td>
<td>0.0160(3)</td>
</tr>
<tr>
<td>O2</td>
<td>0.46540(18)</td>
<td>1.03244(17)</td>
<td>0.41571(6)</td>
<td>0.0179(3)</td>
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<tr>
<td>N1</td>
<td>0.4625(2)</td>
<td>0.74188(19)</td>
<td>0.49075(7)</td>
<td>0.0155(4)</td>
</tr>
<tr>
<td>N2</td>
<td>0.3471(2)</td>
<td>1.04282(19)</td>
<td>0.50961(7)</td>
<td>0.0138(3)</td>
</tr>
</tbody>
</table>

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 CCIN₂O₂ 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 [2.0469(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—Cl₁ = 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 3.597(3) 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···O₁₁: H₁₈···O₁₁ = 2.52 Å, C₁₈···O₁₁ = 3.415(3) Å]
with angle at H18 = 163° for symmetry operation i: −1 + y, 2 − x, −1/4 + z], benzyl-C—H···Cl [C26—H26···Cl1ii; 
H26···Cl1ii = 2.83 Å, C26···Cl1ii = 3.691(3) Å, angle at 
H26 = 155° for ii: x, −1 + y, z] and oxinate-C—H···π(NC₅-
oxinate) [C5—H5···π(N2, C12–C16)ii: H5···π(N2,C12–
C16)ii = 2.94 Å, C5···π(N2,C12–C16)ii = 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(oxine)₂Cl. In each of the R = n-Bu [11] and R = Bz [12] 
structures, very similar coordination geometries are noted.

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