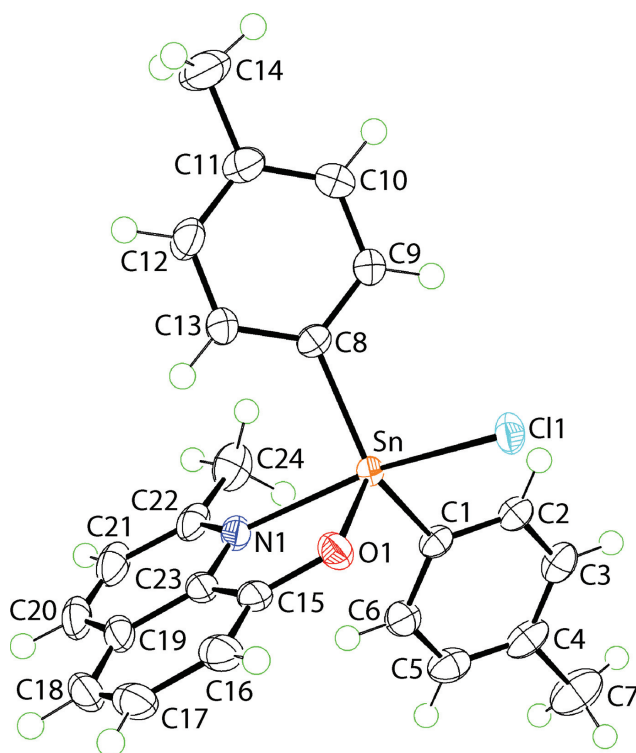


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# Crystal structure of chlorido(2-methylquinolin-8-olato- $\kappa^2N,O$ )-bis(4-tolyl- $\kappa C$ )tin(IV), $C_{24}H_{22}ClNOSn$



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## Abstract

$C_{24}H_{22}ClNOSn$ , monoclinic,  $P2_1/c$  (no. 14),  $a = 13.7584(1)$  Å,  $b = 13.5542(1)$  Å,  $c = 13.0912(1)$  Å,  $\beta = 115.778(1)^\circ$ ,  $V = 2198.36(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{gt}(F) = 0.0170$ ,  $wR_{ref}(F^2) = 0.0448$ ,  $T = 100(2)$  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.

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

|   |  |
|---|--|
| Crystal:  | Colourless prism   |
| Size:   | 0.17 × 0.08 × 0.05 mm                                      |
| Wavelength:   | Cu $K\alpha$ radiation (1.54184 Å)                         |
| $\mu$ :   | 10.5 mm <sup>-1</sup>                                      |
| Diffractometer, scan mode:                            | XtaLAB Synergy, $\omega$                                   |
| $\theta_{max}$ , completeness:                        | 67.1°, >99%  |
| $N(hkl)_{measured}$ , $N(hkl)_{unique}$ , $R_{int}$ : | 28037, 3934, 0.031   |
| Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :             | $I_{obs} > 2\sigma(I_{obs})$ , 3844                        |
| $N(param)_{refined}$ :                                | 256  |
| Programs:   | CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4] |

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

| Atom | x           | y           | z           | $U_{iso}^*/U_{eq}$ |
|------|-------------|-------------|-------------|--------------------|
| Sn   | 0.72920(2)  | 0.64037(2)  | 0.63444(2)  | 0.01363(5)         |
| O1   | 0.86273(10) | 0.63982(8)  | 0.60400(10) | 0.0197(3)          |
| N1   | 0.82987(11) | 0.77392(10) | 0.73685(11) | 0.0187(3)          |
| C1   | 0.75311(13) | 0.56365(12) | 0.78542(13) | 0.0167(3)          |
| C2   | 0.68405(14) | 0.48701(13) | 0.78162(14) | 0.0190(3)          |
| H2   | 0.621472    | 0.473996    | 0.713299    | 0.023*             |
| C3   | 0.70618(15) | 0.42933(14) | 0.87740(15) | 0.0234(4)          |
| H3   | 0.657938    | 0.377950    | 0.874106    | 0.028*             |
| C4   | 0.79841(16) | 0.44632(14) | 0.97795(15) | 0.0249(4)          |
| C5   | 0.86533(15) | 0.52438(14) | 0.98207(14) | 0.0251(4)          |
| H5   | 0.927191    | 0.538126    | 1.050795    | 0.030*             |
| C6   | 0.84329(14) | 0.58265(13) | 0.88735(14) | 0.0211(3)          |
| H6   | 0.889960    | 0.635862    | 0.891953    | 0.025*             |
| C7   | 0.8280(2)   | 0.37843(18) | 1.07858(19) | 0.0394(5)          |
| H7A  | 0.882347    | 0.330887    | 1.080160    | 0.059*             |
| H7B  | 0.763560    | 0.343017    | 1.072220    | 0.059*             |
| H7C  | 0.857471    | 0.417349    | 1.148638    | 0.059*             |
| C8   | 0.60402(13) | 0.73425(13) | 0.52452(13) | 0.0168(3)          |
| C9   | 0.50077(14) | 0.69628(13) | 0.46387(15) | 0.0225(4)          |
| H9   | 0.486346    | 0.629564    | 0.474845    | 0.027*             |
| C10  | 0.41852(15) | 0.75483(14) | 0.38742(15) | 0.0269(4)          |
| H10  | 0.348295    | 0.727760    | 0.347320    | 0.032*             |
| C11  | 0.43723(16) | 0.85235(13) | 0.36861(16) | 0.0239(4)          |
| C12  | 0.54024(15) | 0.89055(14) | 0.43056(16) | 0.0242(4)          |

Table 2 (continued)

| Atom | <i>x</i>    | <i>y</i>    | <i>z</i>    | <i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub> |
|------|-------------|-------------|-------------|---|
| H12  | 0.554276    | 0.957488    | 0.420034    | 0.029*  |
| C13  | 0.62299(14) | 0.83262(13) | 0.50754(15) | 0.0205(3)   |
| H13  | 0.692821    | 0.860127    | 0.548804    | 0.025*  |
| C14  | 0.34981(17) | 0.91637(17) | 0.28329(18) | 0.0370(5)   |
| H14A | 0.282656    | 0.878462    | 0.247722    | 0.056*  |
| H14B | 0.371713    | 0.938123    | 0.224987    | 0.056*  |
| H14C | 0.338319    | 0.974098    | 0.321785    | 0.056*  |
| C15  | 0.93604(13) | 0.71141(13) | 0.64949(13) | 0.0192(3)   |
| C16  | 1.02651(14) | 0.71859(15) | 0.63003(15) | 0.0247(4)   |
| H16  | 1.037420    | 0.672488    | 0.581341    | 0.030*  |
| C17  | 1.10267(15) | 0.79356(16) | 0.68166(16) | 0.0302(4)   |
| H17  | 1.164393    | 0.797085    | 0.666969    | 0.036*  |
| C18  | 1.09071(16) | 0.86170(14) | 0.75250(17) | 0.0312(5)   |
| H18  | 1.144271    | 0.910796    | 0.787588    | 0.037*  |
| C19  | 0.99817(16) | 0.85846(13) | 0.77302(15) | 0.0253(4)   |
| C20  | 0.97390(16) | 0.92612(14) | 0.84113(15) | 0.0308(4)   |
| H20  | 1.022204    | 0.978787    | 0.877451    | 0.037*  |
| C21  | 0.88156(17) | 0.91619(14) | 0.85498(15) | 0.0290(4)   |
| H21  | 0.866043    | 0.962195    | 0.900629    | 0.035*  |
| C22  | 0.80859(15) | 0.83784(13) | 0.80183(14) | 0.0225(4)   |
| C23  | 0.92151(13) | 0.78269(13) | 0.72143(13) | 0.0195(3)   |
| C24  | 0.70778(17) | 0.82378(15) | 0.81613(16) | 0.0291(4)   |
| H24A | 0.646068    | 0.818612    | 0.741396    | 0.044*  |
| H24B | 0.697444    | 0.880267    | 0.857099    | 0.044*  |
| H24C | 0.713527    | 0.763223    | 0.859287    | 0.044*  |
| Cl1  | 0.67328(3)  | 0.49396(3)  | 0.51290(3)  | 0.01955(9)  |

### Source of material

4-Methylphenylmagnesium bromide was prepared from the Grignard reaction of magnesium (Merck) and 4-bromotoluene (Fluka) in tetrahydrofuran. Tetra(4-methylphenyl)tin was synthesised from the reaction of stannic chloride (Fluka) with 4-methylphenylmagnesium bromide in a 1:4 molar ratio. Subsequently, di(4-methylphenyl)tin dichloride was synthesized from the comproportionation reaction of tetra(4-methylphenyl)tin with stannic chloride (Fluka) in a 1:1 molar ratio to obtain a white precipitate. Di(4-methylphenyl)tin dichloride (0.37 g, 1.0 mmol) and 2-methyl 8-quinolinol (Sigma-Aldrich, 0.16 g, 1.0 mmol) were heated in 95% ethanol (30 mL) for 1 h. After filtration, the yellow filtrate was evaporated slowly until colourless crystalline compound was formed. Yield: 0.35 g (70.8%). **M. pt** (Stuart SMP30 digital melting point apparatus; uncorrected): 466–468 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm<sup>-1</sup>): 1505 (m) ν(C=C), 1457 (m) ν(C=N), 1109 (m) ν(C–O). **<sup>1</sup>H NMR** (Bruker Ascend 400 MHz NMR spectrometer; CDCl<sub>3</sub>; ppm relative to Me<sub>4</sub>Si): δ 2.21 (s, 3H, quin-CH<sub>3</sub>), 2.30 (s, 6H, CH<sub>3</sub>), 7.13–7.59 (m, 12H, Ph-H), 8.35 (d, 1H, Ph-H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR): 21.4 (CH<sub>3</sub>), 23.5 (quin-CH<sub>3</sub>), 115.3, 115.9, 123.7, 127.5, 129.3, 129.7, 130.2, 137.5, 139.3, 140.1, 140.5, 155.5, 156.2 (Ph-C).

### Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding with *U*<sub>iso</sub>(H) = 1.2–1.5*U*<sub>eq</sub>(C).

### Comment

8-Hydroxyquinolinato (oxine) compounds of diorganotin chlorides, i.e. molecules of the general formula R<sub>2</sub>Sn(oxine)Cl, adopt three distinct structural motifs in their crystals, despite their being only four examples. Two examples, i.e. with R = Et [5] and 2-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> [6], feature an *N,O*-chelated oxine anion and a penta-coordinate *cis*-C<sub>2</sub>ClNO donor set. In the case when R = MeOC(=O)CH<sub>2</sub>CH<sub>2</sub> [7], i.e. where there is additional coordination potential in the Sn-bound R groups, indeed, one of the carbonyl-O forms a bond with the Sn atom to increase the coordination number to six. The resultant C<sub>2</sub>ClNO<sub>2</sub> donor set defines a skew-trapezoidal bipyramidal geometry with the Sn-bound C atoms lying over the Sn–N and Sn–O(R) bonds [7]. Finally, when the R groups are no longer equivalent, i.e. R = Me and R' = Ph, dimerisation occurs as the phenoxide-O atom bridges two Sn atoms [8]. In this case, the resultant C<sub>2</sub>ClNO<sub>2</sub> donor set defines a distorted octahedral geometry. There appears to be a sole example of related compound with a 2-methyl substituent in the oxine ligand, namely that of Me(Ph)Sn(Meoxine)Cl [9]. Unlike the aforementioned dimeric structure, this is mononuclear and resembles the penta-coordinated, *cis*-C<sub>2</sub>ClNO species above. The present report describes the synthesis and crystal structure determination of a second derivative in the R<sub>2</sub>Sn(Meoxine)Cl series, i.e. (4-tolyl)<sub>2</sub>Sn(Meoxine)Cl, (I), in continuation of related structural studies [10].

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids) and reveals the Sn atom to be penta-coordinated within a *cis*-C<sub>2</sub>ClNO donor set defined by *ipso*-C [Sn–C1 = 2.1285(15) Å and Sn–C8 = 2.1214(16) Å], pyridyl-N [Sn–N1 = 2.3189(14) Å], phenoxide-O [Sn–O1 = 2.0424(12) Å] and Cl [Sn–Cl1 = 2.4489(4) Å] atoms. The coordination geometry is highly distorted with the widest angle of 132.45(6)° corresponding to the C1–Sn–C8 angle and the narrowest angle being the chelate angle, i.e. O1–Sn–N1 = 75.75(5)°. A quantitative assessment of the five-coordinate geometry can be made by calculating the value of τ, which computes to 0.0 for an ideal square-pyramidal geometry and 1.0 for trigonal-bipyramidal [11]. For (I), τ = 0.48, i.e. almost exactly intermediate between the two ideal geometries. Equivalent calculations were performed for Me(Ph)Sn(Meoxine)Cl [9], for which two molecules comprise the asymmetric unit, resulting in τ = 0.38 and 0.56, indicating a tendency to square- and trigonal-bipyramidal geometries, respectively. For completeness, the mononuclear species with oxine, i.e. R = Et [5] and 2-ClC<sub>6</sub>H<sub>4</sub> [6] were evaluated, giving

$\tau = 0.36$  and  $0.33$ , respectively, i.e. indicating distortions towards a square-pyramidal geometry.

In the crystal, the chlorido ligand accepts C–H interactions from a 4-tolyl ring and oxine-methyl [C9–H9 $\cdots$ Cl1<sup>i</sup>: H9 $\cdots$ Cl1<sup>i</sup> = 2.82 Å, C9 $\cdots$ Cl1<sup>i</sup> = 3.621(2) Å with angle at H9 = 142° and C24–H24b $\cdots$ Cl1<sup>ii</sup>: H24b $\cdots$ Cl1<sup>ii</sup> = 2.79 Å, C24 $\cdots$ Cl1<sup>ii</sup> = 3.745(2) Å with angle at H24b = 166° for symmetry operations (i)  $1 - x, 1 - y, 1 - z$  and (ii)  $x, 3/2 - y, 1/2 + z$ ] to generate a supramolecular layer in the *bc*-plane. Layers stack along the *a*-axis without directional interactions between them.

A complimentary analysis of the supramolecular aggregation was conducted by calculating the Hirshfeld surface along with the full and decomposed two-dimensional fingerprint plots, with the use of the program Crystal Explorer 17 [12] and guided by literature protocols [13]. The major contribution to the calculated Hirshfeld surface comes from H $\cdots$ H contacts, at 51.7%. This is followed by H $\cdots$ C/C $\cdots$ H contacts at 30.6% with smaller contributions from H $\cdots$ Cl/Cl $\cdots$ H [12.2%] and H $\cdots$ O/O $\cdots$ H [5.3%].

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