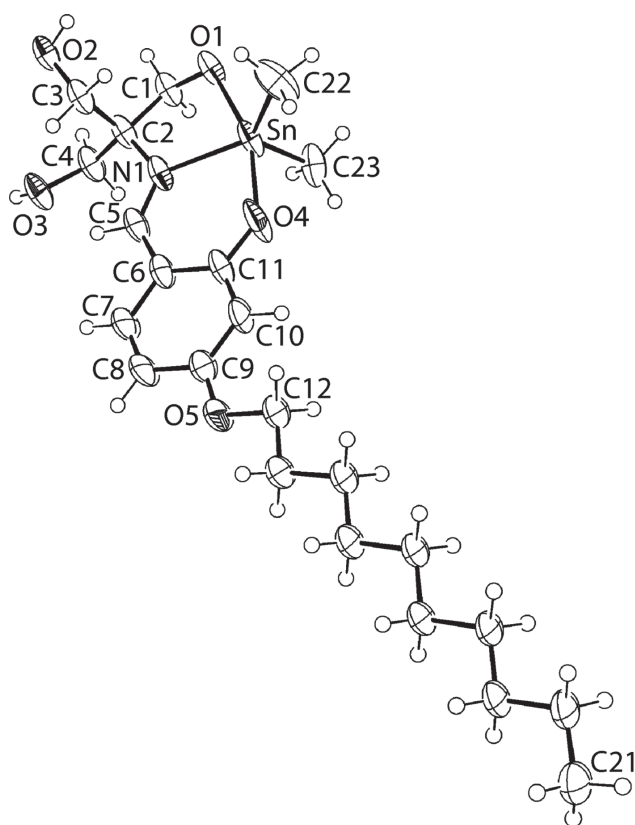


See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink\*

# Crystal structure of (2-([1,1-bis(hydroxymethyl)-2-oxyethyl]iminomethyl)-5-(*n*-decyl)phenolato)-dimethyl-tin(IV), C<sub>23</sub>H<sub>39</sub>NO<sub>5</sub>Sn



CCDC no.: 1948956

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:	Yellow prism
Size:	0.16 × 0.09 × 0.06 mm
Wavelength:	Cu K $\alpha$ radiation (1.54184 Å)
$\mu$ :	8.61 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{\max}$ , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	28723, 4332, 0.070
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 4071
$N(\text{param})_{\text{refined}}$ :	280
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

## Source of material

The melting point of the compound was measured on a Mel-Temp II digital melting point apparatus and was uncorrected. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrophotometer equipped as a Nujol mull in between KBr cell from 4000 to 400 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum was recorded in DMSO-d<sub>6</sub> solution on a Jeol JNM-ECA 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

The Schiff base was synthesized by the 1:1 molar reaction of 4-decyloxy-2-hydroxybenzaldehyde, prepared according to a literature procedure [5], and tris(hydroxymethyl) aminomethane (Tokyo Chemical Industry) in ethanol. Dimethyltin dichloride (Merck, 0.22 g, 1.0 mmol) and the prepared ligand (0.38 g, 1.0 mmol) were heated in 95% ethanol (20 ml) and stirred for 2 h. The filtrate was evaporated slowly until a yellow precipitate was formed. The precipitate was recrystallized from methanol-hexane by slow evaporation to yield yellow crystals.

Yield: 0.18 g (34.1%). **M.pt:** 437–438 K. **IR** (cm<sup>-1</sup>) 3124 (br)  $\nu$ (O–H), 1599 (s)  $\nu$ (C–N), 1529 (*m*)  $\nu$ (C–O), 1066 (s)  $\nu$ (C–O), 1037 (*m*)  $\nu$ (C–O), 756 (w)  $\nu$ (Sn–O), 484 (w)  $\nu$ (Sn–N).

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## Abstract

C<sub>23</sub>H<sub>39</sub>NO<sub>5</sub>Sn, triclinic,  $P\bar{1}$  (no. 2),  $a = 6.0101(2)$  Å,  $b = 9.2999(2)$  Å,  $c = 22.3110(6)$  Å,  $\alpha = 91.482(2)^\circ$ ,  $\beta = 90.594(3)^\circ$ ,  $\gamma = 102.631(2)^\circ$ ,  $V = 1216.28(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{\text{gt}}(F) = 0.0425$ ,  $wR_{\text{ref}}(F^2) = 0.1158$ ,  $T = 100(2)$  K.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
Sn	1.26166(5)	0.48886(3)	0.15157(2)	0.04611(14)
O1	1.4747(5)	0.5106(3)	0.07827(16)	0.0489(7)
O2	1.3614(5)	0.2192(3)	−0.04034(15)	0.0469(7)
H2O	1.413(10)	0.306(3)	−0.050(3)	0.070*
O3	1.3629(6)	−0.0209(3)	0.06142(17)	0.0531(8)
H3O	1.441(10)	−0.083(6)	0.053(3)	0.080*
O4	1.0039(7)	0.3915(3)	0.2107(2)	0.0746(12)
O5	0.4214(7)	0.0664(3)	0.31206(16)	0.0576(9)
N1	1.2376(6)	0.2611(4)	0.12121(18)	0.0429(8)
C1	1.5718(8)	0.3869(5)	0.0695(2)	0.0456(10)
H1A	1.6855	0.3852	0.1018	0.055*
H1B	1.6511	0.3935	0.0307	0.055*
C2	1.3851(7)	0.2442(4)	0.0700(2)	0.0429(10)
C3	1.2370(7)	0.2274(5)	0.0127(2)	0.0445(10)
H3A	1.1150	0.1371	0.0150	0.053*
H3B	1.1630	0.3125	0.0106	0.053*
C4	1.5076(8)	0.1174(5)	0.0769(2)	0.0476(11)
H4A	1.6429	0.1337	0.0510	0.057*
H4B	1.5613	0.1164	0.1190	0.057*
C5	1.1066(8)	0.1430(4)	0.1430(2)	0.0451(10)
H5	1.1204	0.0517	0.1249	0.054*
C6	0.9479(8)	0.1335(5)	0.1896(2)	0.0447(10)
C7	0.8154(10)	−0.0080(5)	0.2031(2)	0.0559(12)
H7	0.8479	−0.0922	0.1830	0.067*
C8	0.6452(11)	−0.0279(5)	0.2433(2)	0.0612(14)
H8	0.5602	−0.1242	0.2511	0.073*
C9	0.5955(9)	0.0963(5)	0.2737(2)	0.0500(11)
C10	0.7212(9)	0.2354(5)	0.2623(2)	0.0502(11)
H10	0.6881	0.3180	0.2835	0.060*
C11	0.8953(8)	0.2576(5)	0.2206(2)	0.0479(11)
C12	0.3428(9)	0.1872(5)	0.3395(2)	0.0510(11)
H12A	0.2969	0.2495	0.3084	0.061*
H12B	0.4654	0.2490	0.3648	0.061*
C13	0.1431(10)	0.1225(5)	0.3771(2)	0.0530(12)
H13A	0.1897	0.0554	0.4060	0.064*
H13B	0.0209	0.0634	0.3509	0.064*
C14	0.0484(10)	0.2401(5)	0.4115(2)	0.0503(11)
H14A	0.1717	0.3014	0.4367	0.060*
H14B	−0.0032	0.3053	0.3825	0.060*
C15	−0.1485(10)	0.1740(5)	0.4509(2)	0.0530(12)
H15A	−0.0965	0.1075	0.4793	0.064*
H15B	−0.2714	0.1133	0.4254	0.064*
C16	−0.2470(10)	0.2864(5)	0.4867(2)	0.0520(12)
H16A	−0.1237	0.3490	0.5115	0.062*
H16B	−0.3039	0.3510	0.4585	0.062*
C17	−0.4393(10)	0.2175(5)	0.5272(2)	0.0518(12)
H17A	−0.3817	0.1537	0.5557	0.062*
H17B	−0.5616	0.1539	0.5024	0.062*
C18	−0.5411(10)	0.3294(5)	0.5627(2)	0.0540(13)
H18A	−0.4190	0.3923	0.5878	0.065*
H18B	−0.5970	0.3939	0.5342	0.065*
C19	−0.7349(10)	0.2608(5)	0.6027(2)	0.0540(12)
H19A	−0.8543	0.1948	0.5779	0.065*
H19B	−0.6774	0.1994	0.6323	0.065*
C20	−0.8419(11)	0.3717(5)	0.6363(2)	0.0587(13)

**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>
H20A	−0.7211	0.4402	0.6597	0.070*
H20B	−0.9047	0.4304	0.6067	0.070*
C21	−1.0289(11)	0.3048(6)	0.6781(2)	0.0617(13)
H21A	−1.1531	0.2403	0.6551	0.093*
H21B	−1.0869	0.3834	0.6985	0.093*
H21C	−0.9685	0.2471	0.7079	0.093*
C22	1.0728(9)	0.6371(6)	0.1185(4)	0.0741(18)
H22A	1.1642	0.7381	0.1227	0.111*
H22B	0.9325	0.6289	0.1414	0.111*
H22C	1.0339	0.6133	0.0761	0.111*
C23	1.5135(9)	0.5553(6)	0.2196(3)	0.0607(14)
H23A	1.6272	0.4943	0.2166	0.091*
H23B	1.4420	0.5433	0.2589	0.091*
H23C	1.5882	0.6590	0.2148	0.091*

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, p.p.m.): δ 0.37 (s, 6H, CH<sub>3</sub>), 0.79 (s, 3H, CH<sub>3</sub>), 1.20–1.70 (m, 16H, CH<sub>2</sub>), 3.85–4.00 (m, 8H, OCH<sub>2</sub>), 6.50 (d, 1H, Ph–H), 7.16 (d, 1H, Ph–H), 7.55–7.58 (m, 1H, Ph–H), 8.29 (s, 1H, N=CH); the OH protons were not observed.

### Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$ . The O-bound H-atoms were located in a difference Fourier map but were refined with a distance restraint of O–H = 0.84 ± 0.01 Å, and with  $U_{\text{iso}}(\text{H})$  set to 1.5 $U_{\text{eq}}(\text{O})$ .

### Comment

Diorganotin Schiff bases derived from tris[(hydroxymethyl)aminomethane] have attracted interest not only owing to their structural diversity but, also due to their good cytotoxic profiles against several human carcinoma cell lines [6]. Herein, the synthesis and crystal and molecular structures of a dimethyltin derivative with a related Schiff base carrying a long side-chain substituent, *n*-decyl, is described as a part of on-going structural studies of these molecules [6–8] along with those of the precursor molecules [9].

The molecular structure is shown in the figure (50% displacement ellipsoids) and features a five-coordinate tin centre, being coordinated by hydroxy-O1, phenoxy-O4, imine-N1 and two methyl atoms. The di-negative Schiff base ligand is tridentate and forms five- and six-coordinate rings. The Sn–O1 bond length [2.074(3) Å] is significantly shorter than the Sn–O4 bond [2.109(4) Å] with the Sn–N1 bond being longer [2.181(3) Å] than each of these. The C5–N1 bond length [1.312(6) Å] is consistent with its status as an imine bond but the relatively short C5–C6 bond [1.410(7) Å] is consistent with significant delocalization of π-electron density over the six-membered ring. These observations are consistent

with the six-membered ring (Sn, O4, N1, C5, C6 & C11) being planar (r.m.s. deviation of 0.026 Å) with the maximum deviation of 0.028(5) Å being for the C6 atom. By contrast, the five-membered ring, defined by the Sn, O1, N1, C1 & C2 atoms, is non-planar, being twisted about the C1–O1 bond. The narrowest angle subtended at the tin atom is found in the O1–Sn–N1 chelate angle of 77.05(13)° whereas the widest, at 159.20(13)°, is found for O1–Sn–O4; the C22–Sn–C23 angle is 121.0(2)°. The five-coordinate geometry defined by the C<sub>2</sub>NO<sub>2</sub> donor set is highly distorted and lies between the the square-pyramidal [ $\tau = 0.0$ ] and trigonal-bipyramidal [ $\tau = 1.0$ ] extremes as indicated by the value of  $\tau = 0.54$ , a well-known geometric measure for five-coordinate geometries [10]. A striking feature of the molecular structure is the presence of the *n*-decyl substituent. This group is slightly kinked with respect to the phenyl ring to which it is bonded, as seen the values of the C12–O5–C9–C10 [6.4(8)°] and C12–O5–C9–C8 [–172.9(5)°] torsion angles. The chain itself adopts an all-*trans* conformation with the torsion angles lying in a narrow range of –177.7(5)°, for C18–C19–C20–C21, to 179.4(4)°, for C16–C17–C18–C19.

The observed coordination geometry for the title compound matches those seen in closely related diorganotin species containing Schiff bases derived from tris [(hydroxymethyl)aminomethane] [6, 7, 11].

In the crystal, each of the hydroxy groups participates in a conventional hydrogen bond with the O2-hydroxyl forming a hydrogen bond to the hydroxy-O1 atom [O2–H20···O1<sup>i</sup>: H20···O1<sup>i</sup> = 1.82(4) Å, O2···O1<sup>i</sup> = 2.654(4) Å with angle at H20 = 175(7)° for symmetry operation (i) 3 – x, 1 – y, –z] and the O3-hydroxyl connecting to the hydroxyl-O2 atom [O3–H30···O2<sup>ii</sup>: H30···O2<sup>ii</sup> = 1.93(6) Å, O3···O2<sup>ii</sup> = 2.771(4) Å with angle at H30 = 175(3)° for (ii) 3 – x, –y, –z]. The hydrogen bonds lead to a supramolecular zigzag chain along the *b* axis direction and the formation of centrosymmetric, 12-membered {···OC<sub>3</sub>OH}<sub>2</sub> synthons. It is noted that the hydroxyl-O3 atom accepts a short intramolecular contact from the imine-C5–H atom [C5–H5···O3: H5···O3 = 2.24 Å, C5···O3 = 2.992(6) Å with angle at H5 = 135°]. The only other intermolecular contact of note, according to the distance criteria in PLATON [12], is a methylene-C–H··· $\pi$ (phenyl) interaction along the *a* axis contributing to the formation of a supramolecular layer in the *ab*-plane. [C4–H4b···Cg(C6–C11)<sup>iii</sup>: H4b···Cg(C6–C11)<sup>iii</sup> = 2.81 Å, C4···Cg(C6–C11)<sup>iii</sup> = 3.793(5) Å with angle at H4b = 173° for (iii) 1 + x, y, z]. The supramolecular layers have the *n*-decyl chains protruding to either side allowing for inter-digitation along the *c* axis.

In order to confirm the importance of hydrophobic interactions in the molecular packing, an analysis of the

calculated Hirshfeld surface was conducted following literature procedures [13] and employing Crystal Explorer 17 [14] for the calculation of the Hirshfeld surfaces and the full and decomposed two-dimensional fingerprint plots. Calculations show that H···H contacts dominate, contributing 74.4% of all contacts to the overall surface. These are followed by H···O/O···H [14.4%] and H···C/C···H [10.2%] contacts, incorporating the O–H···O and C–H··· $\pi$  contacts described above.

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## References

1. Rigaku Oxford Diffraction: CrysAlis<sup>PRO</sup>. Rigaku Corporation, Oxford, UK (2018).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
5. Lai, C. K.; Chang, C.-H.; Tsai, C.-H.: Liquid crystalline properties of bis(salicylaldiminato)copper(II) complexes: the first columnar discotics derived from salicylaldimine. *J. Mater. Chem.* **8** (1998) 599–602.
6. Lee, S. M.; Sim, K. S.; Lo, K. M.: Synthesis, characterization and biological studies of diorganotin(IV) complexes with tris [(hydroxymethyl)aminomethane] Schiff bases. *Inorg. Chim. Acta* **429** (2015) 195–208.
7. Reisi, R.; Misran, M.; Lo, K. M.; Ng, S. W.: (2-[[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-4-chlorophenolato- $\kappa^3N,O,O'$ )dibutyltin(IV). *Acta Crystallogr.* **E66** (2010) m482.
8. Rosely, S. N. B. M.; Hussen, R. S. D.; Lee, S. M.; Halcovitch, N. R.; Jotani, M. M.; Tiekink, E. R. T.: [*N'*-(4-Decyloxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato- $\kappa^3N,O,O'$ ] dimethyltin(IV): crystal structure and Hirshfeld surface analysis. *Acta Crystallogr.* **E73** (2017) 390–396.
9. Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of 2-[[1*E*]-[[1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl]iminiumyl]methyl]-5-(dodecyloxy)benzen-1-olate, C<sub>23</sub>H<sub>39</sub>NO<sub>5</sub>. *Z. Kristallogr. NCS* **234** (2019) submitted. <https://doi.org/10.1515/ncrs-2019-0523>.
10. Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C.: Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]-copper(II) perchlorate. *J. Chem. Soc. Dalton Trans.* (1984) 1349–1356.
11. Lee, S. M.; Ali, H. M.; Lo, K. M.: (2-[[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-4-chlorophenolato- $\kappa^3O,N,O'$ ) dibutyltin(IV). *Acta Crystallogr.* **E66** (2010) m793.
12. Spek, A. L.: Structure validation in chemical crystallography. *Acta Crystallogr.* **D65** (2009) 148–155.

13. Tan, S. L.; Jotani, M. M.; Tiekink, E. R. T.: Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. *Acta Crystallogr.* **E75** (2019) 308–318.
14. Turner, M. J.; McKinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A.: *Crystal Explorer v17*. The University of Western Australia, Australia (2017).