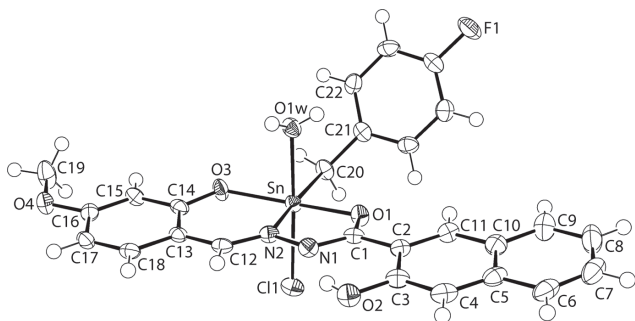


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Crystal structure of aqua-chlorido-(4-fluorobenzyl- κ C)-(N'-(4-methoxy-2-oxidobenzylidene)-3-hydroxy-2-naphthohydrazidato- κ^3 N,O,O')tin(IV), $C_{26}H_{22}ClFN_2O_5Sn$



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Abstract

$C_{26}H_{22}ClFN_2O_5Sn$, triclinic, $P\bar{1}$ (no. 2), $a = 7.1473(6)$ Å, $b = 12.8246(11)$ Å, $c = 13.2899(11)$ Å, $\alpha = 97.541(5)^\circ$, $\beta = 94.503(6)^\circ$, $\gamma = 96.247(5)^\circ$, $V = 1195.13(18)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0325$, $wR_{ref}(F^2) = 0.0756$, $T = 296(2)$ K.

CCDC no.: 1952923

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

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 on a Perkin-Elmer RX1 spectrophotometer as a Nujol mull in a KBr cell from 4000 to 400 cm^{-1} . The ¹H NMR spectrum was recorded in DMSO-*d*₆ solution on a Jeol JNM-ECA 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.32 × 0.28 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.23 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART APEX, ω
θ_{max} , completeness:	28.5°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	12290, 5968, 0.029
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 5146
$N(param)_{refined}$:	335
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

(*E*)-N'-[1-(4-Methoxy-2-hydroxybenzylidene)-3-hydroxy-2-naphthohydrazide] was synthesised from 4-methoxy-2-hydroxybenzaldehyde (Merck) and 3-hydroxy-2-naphthoic hydrazide (Sigma Aldrich) in a 1:1 molar ratio. Di(4-fluorobenzyl)tin dichloride was synthesised by the direct reaction of 4-fluorobenzyl chloride (Merck) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. Di(4-fluorobenzyl)tin dichloride (0.41 g, 1 mmol) and (*E*)-N'-[1-(4-methoxy-2-hydroxybenzylidene)-3-hydroxy-2-naphthohydrazide] (0.34 g, 1 mmol) were dissolved in methanol (25 mL) and refluxed for 3 h. After filtration, the filtrate was evaporated slowly until yellow crystals formed. The crystals were filtered, washed with a minimum amount of methanol-ethanol and air-dried. Yield: 0.10 g (16%). M.pt: 433–435 K. IR (cm^{-1}): 3391 (br) ν (O–H), 1638 ν (C=N), 1603 ν (C=N–N=C), 1032 ν (C–O), 466 ν (Sn–O). ¹H NMR (DMSO-*d*₆, δ (ppm)): δ 2.80 (s, 2H, CH₂), 3.45 (s, 2H, OH₂), 3.88 (s, 3H, OCH₃), 6.70 (d, 1H, $J = 8.80$ Hz, Ph-H), 7.28–7.45 (m, 4H, Ph–H), 7.50–7.66 (m, 4H, Ph–H), 7.73–7.84 (m, 3H, Ph–H), 8.50 (s, 1H, Ph–H), 8.58 (s, 1H, CH), 11.58 (s, 1H, OH).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.93–0.97 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$. The O-bound H-atoms were located in a difference Fourier map but were refined with a distance restraint O–H = 0.82 ± 0.01 Å, and with $U_{iso}(H)$ set to 1.5 $U_{eq}(O)$. Owing to poor agreement, four reflections, i.e. (7 –5 6), (–1 –7 15), (–1 –7 16) and (1 –6 3), were omitted from the final cycles of refinement.

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

Atom	x	y	z	U_{iso}^*/U_{eq}
Sn	0.17145(2)	0.24966(2)	0.56818(2)	0.01331(6)
Cl1	−0.13126(9)	0.29841(5)	0.62791(5)	0.02105(14)
F1	0.8756(2)	0.03862(14)	0.82503(14)	0.0299(4)
N1	0.3158(3)	0.48145(17)	0.57788(17)	0.0161(5)
N2	0.2130(3)	0.39877(17)	0.51106(16)	0.0148(4)
O1	0.3387(3)	0.35449(14)	0.68504(14)	0.0164(4)
O2	0.4360(3)	0.67479(15)	0.64115(15)	0.0198(4)
H2O	0.384(4)	0.6208(16)	0.606(2)	0.030*
O3	0.0639(3)	0.19064(14)	0.42245(14)	0.0189(4)
O4	−0.2405(3)	0.16470(15)	0.08665(14)	0.0196(4)
O1W	0.4512(3)	0.22028(15)	0.50724(14)	0.0178(4)
H1W	0.551(3)	0.232(3)	0.543(2)	0.027*
H2W	0.480(4)	0.250(2)	0.4592(17)	0.027*
C1	0.3754(4)	0.4510(2)	0.6643(2)	0.0146(5)
C2	0.4864(4)	0.5323(2)	0.7409(2)	0.0148(5)
C3	0.5101(4)	0.6420(2)	0.7280(2)	0.0172(5)
C4	0.6047(4)	0.7162(2)	0.8032(2)	0.0206(6)
H4	0.615232	0.787405	0.794661	0.025*
C5	0.6865(4)	0.6866(2)	0.8935(2)	0.0196(6)
C6	0.7898(4)	0.7614(2)	0.9728(2)	0.0253(6)
H6	0.800641	0.833154	0.966730	0.030*
C7	0.8730(4)	0.7291(3)	1.0573(2)	0.0282(7)
H7	0.940992	0.779067	1.107716	0.034*
C8	0.8575(4)	0.6213(3)	1.0693(2)	0.0306(7)
H8	0.915255	0.600506	1.127351	0.037*
C9	0.7574(4)	0.5468(3)	0.9956(2)	0.0269(7)
H9	0.747240	0.475567	1.003914	0.032*
C10	0.6692(4)	0.5778(2)	0.9067(2)	0.0199(6)
C11	0.5662(4)	0.5025(2)	0.8291(2)	0.0171(5)
H11	0.551836	0.431402	0.837789	0.020*
C12	0.1439(4)	0.4228(2)	0.42441(19)	0.0143(5)
H12	0.165175	0.493191	0.413944	0.017*
C13	0.0390(4)	0.3501(2)	0.34483(19)	0.0143(5)
C14	0.0048(4)	0.2392(2)	0.3451(2)	0.0154(5)
C15	−0.0908(4)	0.1751(2)	0.2588(2)	0.0155(5)
H15	−0.114278	0.102223	0.258073	0.019*
C16	−0.1505(4)	0.2206(2)	0.17452(19)	0.0156(5)
C17	−0.1188(4)	0.3304(2)	0.1734(2)	0.0173(5)
H17	−0.160563	0.359826	0.116629	0.021*
C18	−0.0258(4)	0.3929(2)	0.2569(2)	0.0162(5)
H18	−0.004030	0.465642	0.256475	0.019*
C19	−0.2692(5)	0.0518(2)	0.0802(2)	0.0287(7)
H19A	−0.149482	0.025637	0.091030	0.043*
H19B	−0.328514	0.021715	0.013881	0.043*
H19C	−0.348819	0.032369	0.131272	0.043*
C20	0.1733(4)	0.1078(2)	0.6372(2)	0.0177(5)
H20A	0.084865	0.109572	0.688963	0.021*
H20B	0.128522	0.047605	0.585617	0.021*
C21	0.3647(4)	0.0911(2)	0.6855(2)	0.0154(5)
C22	0.4631(4)	0.0114(2)	0.6426(2)	0.0189(6)
H22	0.412135	−0.030848	0.582408	0.023*
C23	0.6378(4)	−0.0063(2)	0.6885(2)	0.0212(6)
H23	0.704526	−0.058998	0.659375	0.025*
C24	0.7070(4)	0.0569(2)	0.7781(2)	0.0199(6)
C25	0.6152(4)	0.1371(2)	0.8232(2)	0.0202(6)
H25	0.666600	0.178642	0.883825	0.024*
C26	0.4434(4)	0.1542(2)	0.7755(2)	0.0182(6)
H26	0.379905	0.208727	0.804021	0.022*

Comment

Organotin compounds have been long-known as potential chemotherapeutic agents for the treatment of a variety of cancers [6]. In this context, molecules related to the title organotin compound with a tridentate hydrazone ligand, have been screened for biological activity [7–9]. In continuation of these and structural studies of these organotin hydrazone species [10–13], the title compound, (I), was investigated by X-ray crystallography.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids). The tin atom is coordinated by the di-negative, tridentate ligand, *via* the oxide-O1, phenoxide-O3 and imine-N2 atoms, a chlorido ligand, a methylene-carbon atom of the organic substituent and a water ligand. The resultant coordination geometry is based on an octahedron with the three *trans* angles deviating significantly from the ideal 180° angle: O1–Sn–O3 = 156.75(7)°, N2–Sn–C20 = 171.06(9)° and Cl1–Sn–O1w = 174.40(5)°. The O,N,O donor atoms of the tridentate ligand occupy meridional positions in the octahedral environment. Deviations are largely related to the acute chelate angles formed in the five-membered, O1–Sn–N2 = 74.21(8)°, and six-membered, O3–Sn–N2 = 84.92(8)°, rings. The Sn–O3(phenoxide) bond length [2.0419(18) Å] is considerably shorter than the Sn–O1(oxide) distance [2.1117(18) Å] and this difference is reflected in the associated C1–O1 [1.306(3) Å] and C14–O3 [1.334(3) Å] bond lengths. Considering the bonding character over the O1–C1–N1–N2–C12 chromophore, the C1–N1 bond [1.315(3) Å] is comparatively short and is only marginally longer than the formally C12–N2 imine bond [1.304(3) Å]. These observations suggest considerable delocalisation of π -electron density over this chromophore; the Sn–Cl1, Sn–N2, Sn–C20 and Sn–O1w bond lengths are 2.4770(7), 2.148(2), 2.143(3) and 2.266(2) Å, respectively. The five-membered chelate ring is planar with the r.m.s. deviation of the five fitted atoms being 0.011 Å. By contrast, the six-membered ring is best described as having an envelope conformation with the O3 atom lying 0.196(3) Å out of the plane defined by the remaining five atoms [r.m.s. deviation = 0.052 Å]; the r.m.s. deviation of the six atoms comprising the chelate ring = 0.075 Å. The dihedral angle between the best planes through the chelate rings is 6.15(8)°, indicating that the rings are almost co-planar. The dihedral angle between the five-membered ring and the least-squares plane through the appended naphthyl ring = 9.30(9)°, a relationship that allows for the formation of an intramolecular hydroxyl-O–H···N(hydrazone) hydrogen bond [O2–H2o···N1: H2o···N1 = 1.78(2) Å, O2···N1 = 2.543(3) Å with angle at H2o = 154(2)°]. The dihedral angle between the six-membered ring and attached phenyl ring is 3.55(9)°, also consistent with a co-planar relationship. Finally, the dihedral

angle between each of the best planes through the five- and six-membered chelate rings and that through the benzyl ring are 58.57(8) and 62.36(8)°, respectively, indicating a splayed disposition.

The presence of a N,O,O tridentate ligand, with the pendent hydroxy group as in (I), with tin bound to chloride, an organic substituent and a water molecule is a rare structural motif, being observed once previously, namely in aqua-(*n*-butyl)-chlorido-(2-hydroxy-*N*-(2-oxy-3-methoxybenzylidene)benzenecarbohydrazonato)tin(IV), isolated as an ethanol solvate [14].

The most prominent supramolecular contacts in the molecular packing are aqua-O—H···Cl [O1w—H1w···Clⁱ: H1w···Clⁱ = 2.47(2) Å, O1w···Clⁱ = 3.265(2) Å with angle at H1w = 167(3)° for symmetry operation (i) 1 + *x*, *y*, *z*] and aqua-O—H···O(hydroxy) [O1w—H2w···Oⁱⁱ: H2w···Oⁱⁱ = 1.85(2) Å, O1w···Oⁱⁱ = 2.657(3) Å with angle at H2w = 174(2)° for (ii) 1 - *x*, 1 - *y*, 1 - *z*]. These combine to give rise to a double chain, with a linear topology along the *a*-axis. The phenyl ring of the benzyl substituent is folded towards the water molecule and shields the water-oxygen atom from participating in an additional (acceptor) hydrogen bonding interaction. The chains are linked into a double layer in the *ab*-plane by very weak methyl-C—H···F interactions [C19—H19a···Fⁱⁱⁱ: H19a···Fⁱⁱⁱ = 2.45 Å, C19···Fⁱⁱⁱ = 3.374(4) Å with angle at H19a = 161° for (iii) 1 - *x*, -*y*, 1 - *z*]. While there are π···π stacking and C—H···π interactions apparent in the packing, these occur within the layers, which stack along the *c*-axis direction without directional interactions between them.

To analyse the molecular packing further, an analysis of the calculated Hirshfeld surfaces along with two-dimensional (overall and delineated) fingerprint plots ensued, using Crystal Explorer 17 [15] following standard procedures [16]. The most dominant contacts contributing to the surface are those involving hydrogen, accounting for nearly 90% of all contacts. Important contributions come from C···H/H···C [23.5%], O···H/H···O [11.4%], Cl···H/H···Cl [9.8%] and F···H/H···F [7.8%] contacts but, the prevalent contacts are of the type H···H [35.9%]. The next most important contacts are of the type O···C/C···O [2.6%].

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References

1. Rigaku Oxford Diffraction: CrysAlis^{PRO}. Rigaku Corporation, Oxford, UK (2018).

- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
- Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
- Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
- Sisido, K.; Takeda, Y.; Kinugawa, Z.: Direct synthesis of organotin compounds I. di- and tribenzyltin chlorides. *J. Am. Chem. Soc.* **83** (1961) 538–541.
- Gielen, M.; Tiekink, E. R. T.: *Metallotherapeutic drugs and metal-based diagnostic agents: the use of metals in medicine.* John Wiley & Sons Ltd: Chichester, England (2005) p. 421–439.
- Lee, S. M.; Ali, H. M.; Sim, K. S.; Malek, S. N. A.; Lo, K. M.: Synthesis, characterization and biological activity of diorganotin complexes with ONO tridentate Schiff base. *Inorg. Chim. Acta* **406** (2013) 272–278.
- Lee, S. M.; Ali, H. M.; Sim, K. S.; Malek, S. N. A.; Nurestri, S.; Lo, K. M.: Synthesis, structural characterization and *in vitro* cytotoxicity of diorganotin complexes with Schiff base ligands derived from 3-hydroxy-2-naphthoylethylhydrazide. *Appl. Organomet. Chem.* **26** (2012) 310–319.
- Hong, M.; Geng, H.; Niu, M.; Wang, F.; Li, D.; Liu, J.; Yin, H.: Organotin(IV) complexes derived from Schiff base *N'*-[(1*E*)-(2-hydroxy-3-methoxyphenyl)methylidene]-pyridine-4-carbohydrazone: synthesis, *in vitro* cytotoxicities and DNA/BSA interaction. *Eur. J. Med. Chem.* **86** (2014) 550–561.
- Rosely, S. N. B. M.; Hussien, R. S. D.; Lee, S. M.; Halcovitch, N. R.; Jotani, M. M.; Tiekink, E. R. T.: [*N'*-(4-Decyloxy-2-oxidobenzylidene)-3-hydroxy-2-naphthoylethylidene]-κ³*N,O,O'*dimethyltin(IV): crystal structure and Hirshfeld surface analysis. *Acta Crystallogr.* **E73** (2017) 390–396.
- Lee, S. M.; Halcovitch, N. R.; Jotani, M. M.; Tiekink, E. R. T.: *N'*-[1-(5-Bromo-2-hydroxyphenyl)ethylidene]isonicotinohydrazide monohydrate: crystal structure and Hirshfeld surface analysis. *Acta Crystallogr.* **E73** (2017) 630–636.
- Lee, S. M.; Halcovitch, N. R.; Tiekink, E. R. T.: Crystal structure of chlorido-methanol-(*N*-(2-(oxy)-3-methoxybenzylidene)pyridine-4-carbohydrazonato-κ³*O,N,O'*)-(4-methylphenyl)methyl-tin(IV), C₂₃H₂₄ClN₃O₄Sn. *Z. Kristallogr. NCS* **233** (2018) 519–521.
- Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of benzyl-chlorido-(4-chloro-*N*-[(2-oxidophenyl)methylidene]benzenecarbohydrazonato)-methanol-tin(IV), C₂₂H₂₀Cl₂N₂O₃Sn. *Z. Kristallogr. NCS* **235** (2019) 121–124.
- Hong, M.; Chang, G.; Li, R.; Niu, M.: Anti-proliferative activity and DNA/BSA interactions of five mono- or di-organotin(IV) compounds derived from 2-hydroxy-*N'*-[(2-hydroxy-3-methoxyphenyl)methylidene]-benzohydrazone. *New J. Chem.* **40** (2016) 7889–7900.
- 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).
- 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.