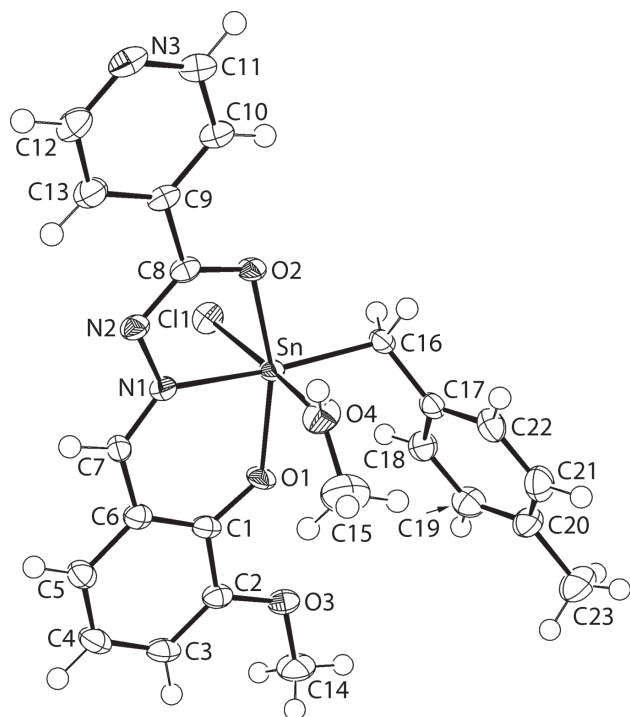


Lee See Mun, Nathan R. Halcovitch and Edward R.T. Tiekink*

Crystal structure of chlorido-methanol-(*N*-(2-(oxy)-3-methoxybenzylidene)pyridine-4-carbohydrazonato- $\kappa^3 O, N, O'$)-(4-methylphenyl)methyl-tin(IV), $C_{23}H_{24}ClN_3O_4Sn$



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Abstract

$C_{23}H_{24}ClN_3O_4Sn$, triclinic, $P\bar{1}$ (no. 2), $a = 9.7536(2)$ Å, $b = 10.0755(2)$ Å, $c = 12.4215(3)$ Å, $\alpha = 84.928(2)^\circ$, $\beta = 72.544(2)^\circ$, $\gamma = 74.382(2)^\circ$, $V = 1121.44(4)$ Å³, $Z = 2$, $R_{gt}(F) = 0.021$, $wR_{ref}(F^2) = 0.054$, $T = 100(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement

*Corresponding author: Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my

Lee See Mun: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Nathan R. Halcovitch: Department of Chemistry, Lancaster University, Lancaster LA1 4YB, United Kingdom

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.23 × 0.19 × 0.15 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	104.6 cm ⁻¹
Diffractometer, scan mode:	SuperNova Dual, ω scans
$2\theta_{max}$, completeness:	148.2°, 98.8%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	39556, 4504, 0.027
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4499
$N(param)_{refined}$:	295
Programs:	Rigaku programs [1], SHELX [2, 3], ORTEP [4]

method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

The N/O-ligand was prepared from the reaction of a 1:1 molar ratio of isonicotinic hydrazide (Aldrich; 0.14 g, 1 mmol) with *o*-vanillin (Fluka; 0.15 g, 1 mmol) in methanolic solution. The obtained ligand was purified and used in the preparation of the title compound. Triethylamine (Merck; 0.14 mL, 1 mmol) was added to a methanolic solution (5 mL) of the aforementioned ligand (0.28 g, 1 mmol) and stirred. After 0.5 h, di(*p*-methylbenzyl)tin dichloride ([5]; 0.40 g, 1 mmol) was added to the reaction mixture. The mixture was refluxed for 3.5 h. Dark-red precipitates were obtained upon slow evaporation of the solution. These were washed with *n*-hexane and recrystallized from its methanol solution. Orange crystals of the title compound were obtained from the slow evaporation of the solution.

Yield: 55%; **M.p.:** 453 K. **IR** (KBr, cm⁻¹): 1618, 1592 (s, C=N–N=C), 580 (w, Sn–O), 477 (w, Sn–N). **¹H NMR** (d₆-DMSO): 1.24 (s, 3H, CCH₃); 2.12 (s, 2H, –CH₂–); 3.17 (s, 3H, methanol-CH₃); 3.71 (s, 1H, –OH); 3.85 (s, 3H, OCH₃); 6.72–6.80 (m, 1H, aromatic H); 6.94–7.18 (m, 4H, aromatic H); 7.24–7.36 (m, 2H, aromatic H); 7.82–7.95 (m, 2H, NCH₂CH₂–); 8.72–8.80 (m, 2H, NCH₂CH₂–); 8.91 (s, 1H, HC=N).

Experimental details

The carbon-bound hydrogen atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5 U_{eq}(C)$. The O-bound H-atom was located

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Sn	0.29355(2)	0.70396(2)	0.25825(2)	0.01324(5)
Cl1	0.55846(6)	0.69779(5)	0.18538(4)	0.02092(11)
O1	0.32651(17)	0.51058(15)	0.32588(13)	0.0185(3)
O2	0.24035(17)	0.86474(14)	0.14459(12)	0.0160(3)
O3	0.36102(17)	0.30280(15)	0.46163(13)	0.0195(3)
O4	0.05359(18)	0.70959(17)	0.30173(14)	0.0236(3)
H4O	0.001(3)	0.758(3)	0.264(2)	0.035 [*]
N1	0.30655(19)	0.60406(18)	0.10720(15)	0.0144(3)
N2	0.27872(19)	0.69127(18)	0.01851(15)	0.0157(3)
N3	0.1147(2)	1.1219(2)	−0.19068(16)	0.0208(4)
C1	0.3550(2)	0.3883(2)	0.28095(18)	0.0152(4)
C2	0.3760(2)	0.2713(2)	0.35355(18)	0.0161(4)
C3	0.4073(2)	0.1397(2)	0.3134(2)	0.0197(4)
H3	0.4226	0.0629	0.3625	0.024 [*]
C4	0.4168(2)	0.1177(2)	0.2013(2)	0.0210(4)
H4	0.4382	0.0267	0.1747	0.025 [*]
C5	0.3951(2)	0.2283(2)	0.13011(19)	0.0185(4)
H5	0.4011	0.2136	0.0541	0.022 [*]
C6	0.3636(2)	0.3647(2)	0.16896(18)	0.0155(4)
C7	0.3377(2)	0.4729(2)	0.08839(18)	0.0150(4)
H7	0.3438	0.4463	0.0152	0.018 [*]
C8	0.2469(2)	0.8205(2)	0.04751(17)	0.0147(4)
C9	0.2094(2)	0.9257(2)	−0.03801(18)	0.0155(4)
C10	0.1645(2)	1.0650(2)	−0.01213(19)	0.0181(4)
H10	0.1652	1.0953	0.0579	0.022 [*]
C11	0.1187(2)	1.1589(2)	−0.0910(2)	0.0210(4)
H11	0.0888	1.2542	−0.0734	0.025 [*]
C12	0.1630(3)	0.9873(2)	−0.21647(19)	0.0218(5)
H12	0.1633	0.9600	−0.2878	0.026 [*]
C13	0.2123(2)	0.8867(2)	−0.14371(19)	0.0204(4)
H13	0.2476	0.7926	−0.1654	0.024 [*]
C14	0.3818(3)	0.1893(2)	0.5372(2)	0.0276(5)
H14A	0.3079	0.1375	0.5432	0.041 [*]
H14B	0.3698	0.2235	0.6118	0.041 [*]
H14C	0.4819	0.1289	0.5086	0.041 [*]
C15	−0.0154(3)	0.6146(3)	0.3713(3)	0.0373(6)
H15A	0.0510	0.5217	0.3572	0.056 [*]
H15B	−0.1083	0.6175	0.3547	0.056 [*]
H15C	−0.0370	0.6382	0.4506	0.056 [*]
C16	0.2458(3)	0.8323(2)	0.40043(17)	0.0176(4)
H16A	0.3362	0.8619	0.3964	0.021 [*]
H16B	0.1674	0.9162	0.3943	0.021 [*]
C17	0.1961(2)	0.7673(2)	0.51367(18)	0.0169(4)
C18	0.2971(2)	0.6724(2)	0.56028(19)	0.0200(4)
H18	0.3992	0.6466	0.5185	0.024 [*]
C19	0.2510(3)	0.6155(2)	0.6658(2)	0.0226(5)
H19	0.3217	0.5511	0.6955	0.027 [*]
C20	0.1018(3)	0.6511(2)	0.72981(19)	0.0229(5)
C21	0.0010(3)	0.7445(2)	0.6832(2)	0.0238(5)
H21	−0.1011	0.7698	0.7249	0.029 [*]
C22	0.0473(2)	0.8013(2)	0.57677(19)	0.0207(4)
H22	−0.0237	0.8645	0.5466	0.025 [*]
C23	0.0524(3)	0.5874(3)	0.8451(2)	0.0341(6)
H23A	−0.0534	0.6292	0.8800	0.051 [*]
H23B	0.1102	0.6038	0.8926	0.051 [*]
H23C	0.0685	0.4880	0.8375	0.051 [*]

in a difference Fourier map but was refined with a distance restraint of O–H = 0.84 ± 0.01 Å, and with *U*_{iso}(H) set to 1.5 *U*_{eq}(O). Owing to poor agreement, the (6̄ 5 7) reflection was omitted from the final cycles of refinement.

Comment

In the field of bioinorganic chemistry, many hydrazone ligands and their metal complexes have been screened for biological activity and among these, organotin(IV) hydrazone compounds are of significant interest for their potential anti-tumour and anti-microbial activities [6–8]. It was in this context that the title compound, BnSn(L)Cl[O(H)Me], where LH₂ is *N*-[(1*Z*)-(2-hydroxy-3-methoxyphenyl)methylidene]pyridine-4-carbohydrazonic acid, was characterized.

As indicated in the figure (70% displacement ellipsoids), the tin(IV) centre is octahedrally coordinated within a CCINO₃ donor set defined by the N,O,O' atoms of the dinegative, tridentate Schiff base ligand, the chloride atom, the benzyl-carbon atom and an oxygen atom derived from a methanol molecule. The chlorido ligand occupies a position *trans* to the methanol-oxygen atom. The mode of coordination of the Schiff base ligand leads to the formation of five- and six-membered chelate rings. The SnON₂C ring is strictly planar with a r.m.s. deviation of 0.0091 Å, whereas the SnONC₃ ring is less planar with a r.m.s. of 0.0276 Å; the maximum deviations above and below the plane are found for the Sn [0.0374(8) Å] and N1 [0.0339(12) Å] atoms, respectively. While to a first approximation the entire Schiff base ligand is planar, there is a twist of 9.57(7)° between the pendant 4-pyridyl ring and the best plane through the remaining C₈N₂O₂ atoms [r.m.s. deviation = 0.0323 Å]. The phenyl ring of the tin-bound organo substituent is folded towards the methoxyphenyl ring and is approximately orthogonal to the best plane through the C₈N₂O₂ atoms, forming a dihedral angle of 70.21(5)°.

Schiff base ligands related to that in the title compound have attracted the interest of the crystal engineering community owing to the possibility of secondary interactions between the pendant pyridyl-N atom and other Lewis acid centres [9, 10]. In the present case, this does not occur as the tin(IV) atom is coordinated to a methanol-O atom instead. However, the pyridyl-N atom accepts a conventional methanol-O–H···N(pyridyl) hydrogen bond from the coordinated methanol molecule [O4–H4o···N3ⁱ = 1.80(3) Å and 174(3)° for i: −*x*, 2 − *y*, −*z*]. These interactions occur between centrosymmetrically molecules to form dimeric aggregates. These, in turn, are connected by non-classical imine-C–H···Cl interactions [C7–H7···Cl1ⁱⁱ = 2.77 Å and 161° for ii: 1 − *x*, 1 − *y*, −*z*], again between centrosymmetrically related molecules. The result of the aforementioned intermolecular interactions is the formation of a supramolecular chain aligned along the [1 1̄ 0] direction.

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