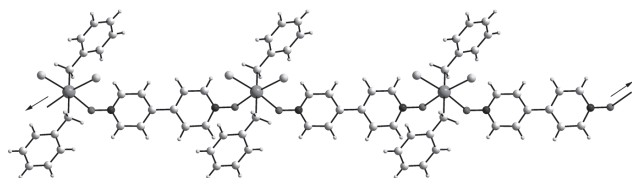
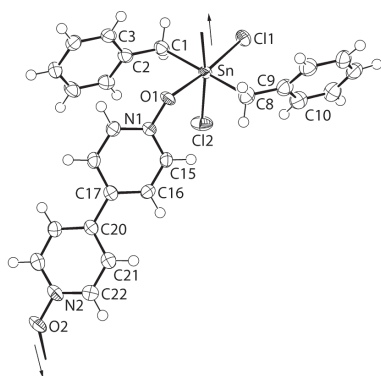




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Crystal structure of *catena*-poly[dibenzyl-dichlorido-(μ_2 -[4,4'-bipyridine]1,1'-dioxide- κ^2 O:O')tin(IV)], $C_{24}H_{22}Cl_2N_2O_2Sn$



<https://doi.org/10.1515/ncrs-2019-0529>

Received July 25, 2019; accepted August 25, 2019; available online September 11, 2019

Abstract

$C_{24}H_{22}Cl_2N_2O_2Sn$, monoclinic, $P2_1/n$ (no. 14), $a = 12.6418(1)$ Å, $b = 13.2422(1)$ Å, $c = 13.6364(1)$ Å, $\beta = 104.6370(10)^\circ$, $V = 2208.72(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0292$, $wR_{ref}(F^2) = 0.0778$, $T = 100(2)$ K.

CCDC no.: 1949157

The asymmetric unit 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.

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Table 1: Data collection and handling.

Crystal:	Pale-yellow prism
Size:	$0.12 \times 0.08 \times 0.06$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	11.6 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1° , $>99\%$
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	27187, 3936, 0.034
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3775
$N(param)_{refined}$:	280
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

General: The melting point of the compound was measured on a Electrothermal digital melting point apparatus and was uncorrected. The elemental analysis was performed on a Perkin-Elmer EA2400 CHN analyser. 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.

Synthesis: Dibenzyltin dichloride was synthesized by the direct reaction of benzyl chloride (Merck) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. Dibenzyltin dichloride (0.37 g, 1 mmol) and 4,4'-bipyridine *N,N'*-dioxide di-hydrate (Sigma Aldrich, 0.11 g, 0.5 mmol) were dissolved in methanol (25 mL) and the mixture was refluxed for 2 h. After filtration, the filtrate was evaporated slowly until pale-yellow crystals were formed. The crystals were filtered, washed with a minimum amount of ethanol and air-dried. Yield: 0.34 g (60.7%). **M.pt:** 469–471 K. **Anal. Calc.** for $C_{24}H_{22}Cl_2N_2O_2Sn$: C 51.33; H 3.92; N 4.99%. Found: C 50.79; H 3.74; N 4.94%. **¹H NMR** (DMSO-*d*₆, ppm): δ 2.97 (s, 4H, CH₂), 7.03–7.23 (m, 10H, Ph–H), 7.86 (d, 4H, $J = 7.00$ Hz, py–H), 8.30 (d, 4H, $J = 7.10$ Hz, py–H).

Experimental details

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

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

Atom	x	y	z	U _{iso} ^a /U _{eq}
Sn	1.09475(2)	0.67803(2)	0.28008(2)	0.01789(9)
Cl1	1.22684(6)	0.77789(6)	0.21009(6)	0.02686(18)
Cl2	0.93154(7)	0.78270(7)	0.19579(7)	0.0325(2)
O1	0.99395(17)	0.57416(17)	0.35776(16)	0.0199(5)
O2	0.23344(18)	0.57747(19)	0.37477(19)	0.0272(5)
N1	0.8900(2)	0.58326(19)	0.36099(19)	0.0171(5)
N2	0.3382(2)	0.5819(2)	0.3729(2)	0.0219(6)
C1	1.1330(3)	0.7773(3)	0.4097(3)	0.0237(7)
H1A	1.2134	0.7768	0.4370	0.028*
H1B	1.1124	0.8466	0.3849	0.028*
C2	1.0831(3)	0.7581(3)	0.4958(2)	0.0225(7)
C3	1.1323(3)	0.6927(3)	0.5746(3)	0.0230(7)
H3	1.1988	0.6599	0.5734	0.028*
C4	1.0855(3)	0.6750(3)	0.6545(3)	0.0246(7)
H4	1.1197	0.6297	0.7069	0.030*
C5	0.9887(3)	0.7228(3)	0.6586(3)	0.0252(7)
H5	0.9570	0.7108	0.7138	0.030*
C6	0.9392(3)	0.7881(3)	0.5815(3)	0.0273(7)
H6	0.8728	0.8207	0.5834	0.033*
C7	0.9858(3)	0.8062(3)	0.5015(3)	0.0255(7)
H7	0.9514	0.8520	0.4495	0.031*
C8	1.0598(3)	0.5557(3)	0.1677(3)	0.0288(8)
H8A	1.0825	0.4914	0.2038	0.035*
H8B	0.9796	0.5526	0.1397	0.035*
C9	1.1110(3)	0.5609(3)	0.0812(3)	0.0265(7)
C10	1.0816(3)	0.6372(3)	0.0091(3)	0.0291(8)
H10	1.0263	0.6840	0.0143	0.035*
C11	1.1315(3)	0.6461(3)	-0.0702(3)	0.0306(8)
H11	1.1102	0.6986	-0.1186	0.037*
C12	1.2110(3)	0.5795(3)	-0.0786(3)	0.0284(8)
H12	1.2485	0.5883	-0.1302	0.034*
C13	1.2369(3)	0.4994(3)	-0.0123(3)	0.0276(7)
H13	1.2884	0.4504	-0.0216	0.033*
C14	1.1884(3)	0.4899(3)	0.0678(3)	0.0283(7)
H14	1.2077	0.4351	0.1138	0.034*
C15	0.8096(3)	0.5919(2)	0.2746(2)	0.0196(6)
H15	0.8281	0.5969	0.2114	0.024*
C16	0.7021(3)	0.5934(2)	0.2770(2)	0.0212(7)
H16	0.6467	0.5993	0.2156	0.025*
C17	0.6732(3)	0.5864(2)	0.3695(2)	0.0181(6)
C18	0.7587(3)	0.5812(2)	0.4574(2)	0.0205(6)
H18	0.7426	0.5795	0.5217	0.025*
C19	0.8656(3)	0.5787(2)	0.4519(2)	0.0204(6)
H19	0.9227	0.5738	0.5123	0.024*
C20	0.5574(3)	0.5845(2)	0.3723(2)	0.0183(6)
C21	0.4770(3)	0.5466(3)	0.2904(3)	0.0242(7)
H21	0.4976	0.5212	0.2327	0.029*
C22	0.3689(3)	0.5456(3)	0.2920(3)	0.0257(7)
H22	0.3155	0.5192	0.2359	0.031*
C23	0.4127(3)	0.6178(3)	0.4542(3)	0.0235(7)
H23	0.3898	0.6425	0.5109	0.028*
C24	0.5223(3)	0.6188(2)	0.4555(2)	0.0209(7)
H24	0.5744	0.6431	0.5136	0.025*

Comment

Crystal structure determinations of neutral organotin compounds of 4,4'-bipyridine *N,N'*-dioxide (L; systematic name: [4,4'-bipyridine]1,1'-dioxide) are rare, being restricted to the *cis*- and *trans*-isomers of octahedral (4-fluorobenzyl)₂SnCl₂(L) [6]. Each of these is a one-dimensional coordination polymer with the topology being dependent on the specific isomer. Thus, while *trans*-isomer gives rise to a linear chain, the topology of the chain formed by the *cis*-isomer is helical [6]. In continuation of these structural studies, the title compound, also a coordination polymer, [benzyl₂SnCl₂(L)]_n, (I), was investigated by X-ray crystallographic methods.

The molecular structure of the asymmetric unit of (I) is shown in the upper view of the figure (70% displacement ellipsoids). The coordination geometry is based on an octahedron with the donor set defined by two methylene-carbon atoms of the benzyl substituents, two chlorido ligands and two oxido-oxygen atoms derived from two different 4,4'-bipyridine *N,N'*-dioxide molecules, each of which is bidentate bridging. The *cis*-disposed Sn—Cl bond lengths are disparate with Sn—Cl1 of 2.5007(8) Å being shorter than Sn—Cl2 of 2.5101(8) Å. This is despite the oxido-oxygen atoms are each *trans* to a chloride [Cl1—Sn—O1 = 172.02(6)° and Cl2—Sn—O2ⁱ = 172.33(6)° for symmetry operation (i) 1 + x, y, z] form experimentally equivalent Sn—O bonds, i.e. Sn—O1 = 2.306(2) Å and Sn—O2ⁱ = 2.317(2) Å. In the same way, non-systematic variations are noted in the Sn—C bond lengths, with Sn—C1 of 2.157(3) Å being shorter than Sn—C8 of 2.196(3) Å; C1—Sn—C8 = 170.03(14)°. Non-systematic variations in geometric parameters are notorious in organotin chemistry and DFT calculations indicate these arise as a result of the crystalline manifold rather than any chemical reasons [7, 8]. The maximum deviation from a regular octahedral geometry in terms of *cis*-angles is seen in the O1—Sn—O2ⁱ angle of 80.18(8)°. As seen from the lower part of the figure, the resulting supramolecular chain has a linear topology, being propagated by translational symmetry.

The crystal of (I) features pyridyl-C—H...Cl [C23—H23...Cl2ⁱⁱ: H23...Cl2ⁱⁱ = 2.64 Å, C23...Cl2ⁱⁱ = 3.500(4) Å with angle at H23 = 152° for (ii) -1/2 + x, 3/2 - y, 1/2 + z] and pyridyl-C—H...O(oxido) [C18—H18...O2ⁱⁱⁱ: H18...O2ⁱⁱⁱ = 2.49 Å, C18...O2ⁱⁱⁱ = 3.090(4) Å with angle at H18 = 121° for (iii) 1 - x, 1 - y, 1 - z] interactions which combine with methylene- and pyridyl-C—H...π(phenyl) [C8—H8b...Cg(C9—C14)^{iv}: H8b...Cg(C9—C14)^{iv} = 2.76 Å, C8...Cg(C9—C14)^{iv} = 3.527(4) Å with angle at H8b = 135° and C16—H16...Cg(C2—C7)^v: H16...Cg(C2—C7)^v = 2.94 Å, C16...Cg(C2—C7)^v = 3.709(3) Å with angle at H16 = 138° for (iv) 2 - x, 1 - y, -z and (v) -1/2 + x, 3/2 - y, -1/2 + z] interactions to sustain a three-dimensional architecture.

Employing Crystal Explorer 17 [9] and literature procedures [10], the calculated Hirshfeld surfaces and two-dimensional (full and decomposed) fingerprint plots were obtained. An analysis of this showed that the most significant percentage contributors to the surface are H···H contacts, accounting for 42.9% of all contacts. There are other significant contacts to the surface of the asymmetric unit, namely C···H/H···C [25.3%], Cl···H/H···Cl [16.0%] and O···H/H···H [7.7%]. Of the remaining 8% of surface contacts, the most dominant are N···H/H···N [2.3%].

Acknowledgements: Sunway University Sdn Bhd is thanked for financial support of this work through Grant no. STR-RCTR-RCCM-001-2019.

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