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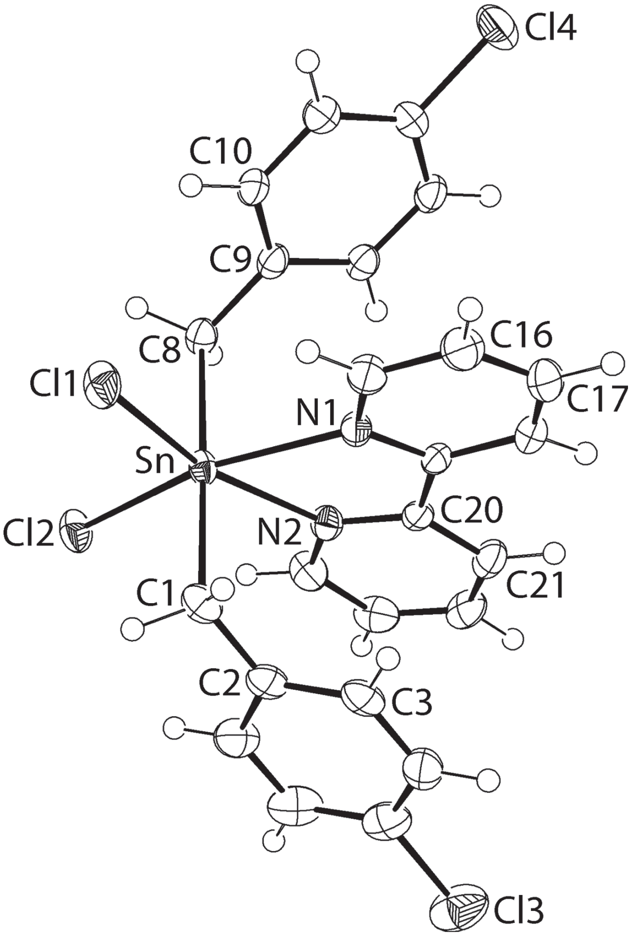
Crystal structure of (2,2′-bipyridyl)bis (4-chlorobenzyl)dichloridotin(IV), $C_{24}H_{20}Cl_4N_2Sn$



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Abstract

$C_{24}H_{20}Cl_4N_2Sn$, monoclinic, $P2_1/n$ (no. 14), $a = 7.7944(1)$ Å, $b = 21.1245(2)$ Å, $c = 14.7611(1)$ Å, $\beta = 95.077(1)°$, $V = 2420.92(4)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0229$, $wR_{ref}(F^2) = 0.0603$, $T = 100(2)$ 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:	$0.14 \times 0.09 \times 0.04$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	12.6 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	30103, 4329, 0.042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3987
$N(param)_{refined}$:	280
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The melting point of the compound was measured on a Melt-Temp II digital melting point apparatus and was uncorrected. The IR spectrum was measured on a Bruker Vertex 70v FTIR spectrophotometer from 4000 to 400 cm^{-1}. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in $CDCl_3$ solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

Di(4-chlorobenzyl)tin dichloride was synthesized by the direct reaction of 4-chlorobenzyl chloride (Aldrich) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. Di(4-chlorobenzyl)tin dichloride (0.44 g, 1.0 mmol) and 2,2′-bipyridine (Aldrich, 0.16 g, 1.0 mmol) were heated in 95% ethanol (30 mL) and stirred for 2 h. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. Yield: 0.31 g (51.9%). **M.pt:** 471–473 K. IR (cm^{-1}): 1606 (m) ν(C—N), 1483, 1141 (s) ν(C—N), 481 (m) ν(Sn—N). **^{1}H NMR** ($CDCl_3$, ppm): δ 3.17 (s, 2H, Ph–CH_2), 6.55–6.56 (dd, 2H, Ph—H), 6.57–6.58 (dd, 2H, Ph—H), 7.50–7.73 (m, 1H, bipy-H), 7.86–7.88 (d, 1H, bipy-H), 8.03–8.07 (t, 1H,

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn	0.56304(2)	0.69771(2)	0.57470(2)	0.02011(6)
Cl1	0.65370(8)	0.76490(3)	0.71076(4)	0.03300(14)
Cl2	0.46362(8)	0.59790(3)	0.64596(4)	0.03040(14)
Cl3	0.98078(10)	0.50596(4)	0.25670(5)	0.0559(2)
Cl4	0.16551(14)	0.98789(4)	0.39746(5)	0.0602(2)
N1	0.6389(2)	0.77422(9)	0.47038(12)	0.0220(4)
N2	0.4981(3)	0.66045(9)	0.42577(13)	0.0237(4)
C1	0.8256(3)	0.66250(12)	0.57962(17)	0.0293(5)
H1A	0.9052	0.6991	0.5846	0.035*
H1B	0.8487	0.6368	0.6354	0.035*
C2	0.8653(3)	0.62366(12)	0.50031(18)	0.0274(5)
C3	0.9441(3)	0.65035(13)	0.42807(17)	0.0295(6)
H3	0.9741	0.6939	0.4302	0.035*
C4	0.9793(3)	0.61458(14)	0.35337(18)	0.0347(6)
H4	1.0346	0.6332	0.3051	0.042*
C5	0.9331(3)	0.55163(14)	0.35000(19)	0.0361(6)
C6	0.8530(3)	0.52352(14)	0.4196(2)	0.0403(7)
H6	0.8211	0.4801	0.4163	0.048*
C7	0.8204(3)	0.55973(13)	0.4940(2)	0.0357(6)
H7	0.7659	0.5406	0.5421	0.043*
C8	0.3035(3)	0.73429(11)	0.57325(16)	0.0245(5)
H8A	0.2244	0.7033	0.5412	0.029*
H8B	0.2731	0.7367	0.6369	0.029*
C9	0.2704(3)	0.79740(11)	0.53029(16)	0.0234(5)
C10	0.2932(3)	0.85329(12)	0.58044(16)	0.0270(5)
H10	0.3307	0.8510	0.6434	0.032*
C11	0.2624(4)	0.91181(13)	0.54036(17)	0.0332(6)
H11	0.2767	0.9495	0.5753	0.040*
C12	0.2103(4)	0.91449(12)	0.44805(18)	0.0338(6)
C13	0.1897(3)	0.86048(13)	0.39608(16)	0.0293(5)
H13	0.1553	0.8632	0.3328	0.035*
C14	0.2197(3)	0.80247(11)	0.43712(17)	0.0245(5)
H14	0.2058	0.7651	0.4015	0.029*
C15	0.7005(3)	0.83109(12)	0.49631(17)	0.0290(5)
H15	0.7154	0.8406	0.5594	0.035*
C16	0.7434(4)	0.87653(13)	0.4348(2)	0.0368(6)
H16	0.7898	0.9162	0.4551	0.044*
C17	0.7174(4)	0.86304(13)	0.3438(2)	0.0408(7)
H17	0.7455	0.8935	0.3000	0.049*
C18	0.6503(4)	0.80501(12)	0.31598(19)	0.0339(6)
H18	0.6292	0.7957	0.2530	0.041*
C19	0.6136(3)	0.76016(11)	0.38062(15)	0.0227(5)
C20	0.5476(3)	0.69619(11)	0.35705(16)	0.0219(5)
C21	0.5388(3)	0.67292(13)	0.26900(16)	0.0301(5)
H21	0.5729	0.6985	0.2208	0.036*
C22	0.4795(3)	0.61185(14)	0.25209(17)	0.0336(6)
H22	0.4758	0.5949	0.1923	0.040*
C23	0.4262(3)	0.57587(13)	0.32175(18)	0.0340(6)
H23	0.3828	0.5343	0.3110	0.041*
C24	0.4377(3)	0.60198(12)	0.40811(18)	0.0307(6)
H24	0.4012	0.5774	0.4568	0.037*

bipy-H), 9.09–9.11 (d, 1H, bipy-H). **^{13}C{^{1}H} NMR** ($CDCl_3$, ppm): δ 50.4 (CH_2), 127.3, 129.1, 129.8, 138.2 (Ph—C), 121.0, 126.6, 127.0, 140.6, 148.5 (bipy-C).

Experimental details

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

Comment

In connection with the recent report of the crystal and molecular structures of (4-$BrC_6H_4)_2SnBr_2$(2,2′-bipyridyl) [6], herein the synthesis and structure of the all-chloro derivative, (I), are described. The molecule of (I) is illustrated in the figure (50% displacement ellipsoids). A distorted octahedral geometry for the tin atom is noted which is based on a $C_2Cl_2N_2$ donor set defined by two carbon atoms of the 4-chloro-substituted benzyl groups, two chloride atoms and two nitrogen atoms of the 2,2′-bipyridyl molecule. The benzyl-carbon atoms are mutually trans, and each of the chloride atoms is trans to a pyridyl-nitrogen atom. The Sn—Cl bond lengths are experimentally equivalent [Sn—Cl1 = 2.5093(6) Å and Sn—Cl2 = 2.5094(6) Å] as are the Sn—N bonds [Sn—N1 = 2.3439(19) Å and Sn—N2 = 2.3478(19) Å]. This contrasts the situation found in the all-bromo derivative where non-systematic differences in tin-ligand bond lengths were noted [6]. Such variations have been proven by DFT methods on related compounds to be dependent upon global molecular packing effects in crystals [7, 8].

In (I), the five-membered chelate ring formed by the 2,2′-bipyridyl ligand is responsible for the greatest distortion from the ideal octahedral geometry with the acute N1—Sn—N2 chelate angle being 70.25(7)°. The maximum deviation of a trans angles is seen in the N1—Sn—Cl2 angle of 163.73(5)°. As reported for the all-bromo derivative [6], the benzyl-phenyl rings are orientated to lie over the 2,2′-bipyridyl molecule. In the present case, the separation between the ring centroids of the chelate and C2-phenyl rings is 3.7784(14) Å; the separation between the N1-pyridyl and C9-phenyl rings is marginally longer at 3.7957(15) Å. Recent literature has highlighted the stabilising effect of $\pi\cdots\pi$ interactions where at least one of the rings is a chelate ring [9, 10].

The structure of the $(4\text{-}ClC_6H_4CH_2)_2SnCl_2$ precursor molecule is available in the literature for comparison [11]. The independent Sn—Cl bond length in this 2-fold symmetric structure is 2.3754(11) Å which is considerably shorter than those reported above for the title compound, reflecting, in part, the increased coordination number for tin.

While the precursor $(4\text{-}XC_6H_4CH_2)_2SnX_2$, X = Cl [11] and Br [12] species are isostructural, those of $(4\text{-}XC_6H_4CH_2)_2SnX_2$(2,2′-bipyridyl), X = Cl and Br [6], are not. However, the title compound appears to be isostructural with the 1,10-phenanthroline analogue [13]. The non-isostructural relationship between the $(4\text{-}XC_6H_4CH_2)_2SnX_2$(2,2′-bipyridyl), X = Cl and Br [6], compounds is reflected in the distinctive atom-to-atom points of contact between molecules.

Based on the distance criteria in PLATON [14], the only significant intermolecular interactions in the crystal are benzyl- and pyridyl-C—H···Cl(tin- and phenyl-bound) interactions [C4—H4···Cl1^{i}: H4···Cl1^{i} = 2.77 Å, C4···Cl1^{i} = 3.642(3) Å with angle at H4 = 153°, and C22—H22···Cl4^{ii}: H22···Cl4^{ii} = 2.80 Å, C22···Cl4^{ii} = 3.545(3) Å with angle at H22 = 136° for symmetry operations (i) 1/2 + x, 3/2 − y, −1/2 + z and (ii) 1/2 − x, −1/2 + y, 1/2 − z]. The molecules pack in columns aligned along the *a*-axis direction and with each molecule accepting and donating two C—H···Cl interactions, a three-dimensional architecture ensues.

Finally, an analysis of the calculated Hirshfeld surfaces was undertaken in order to evaluate the molecular packing further and to make a comparison with the packing in the crystal of the all-bromo analogue [6]. For this purpose, Crystal Explorer 17 [15] was employed following protocols established in the literature [16] to calculate the Hirshfeld surfaces and two-dimensional fingerprint plots (overall and delineated into specific contacts). In the crystal, H···H contacts make the greatest overall contribution at 42.3%, being greater than H···Cl/Cl···H contacts at 38.7%. Other significant contacts are noted, that is, H···C/C···H [12.4%], then Cl···C/C···Cl [3.0%], Cl···Cl [2.2%] and C···C [2.0%]. A very similar pattern in surface contacts were calculated for the all-bromo derivative with the notable exception that H···Br/Br···H [40.8%] were marginally more prevalent than H···H [40.2%] contacts [6].

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