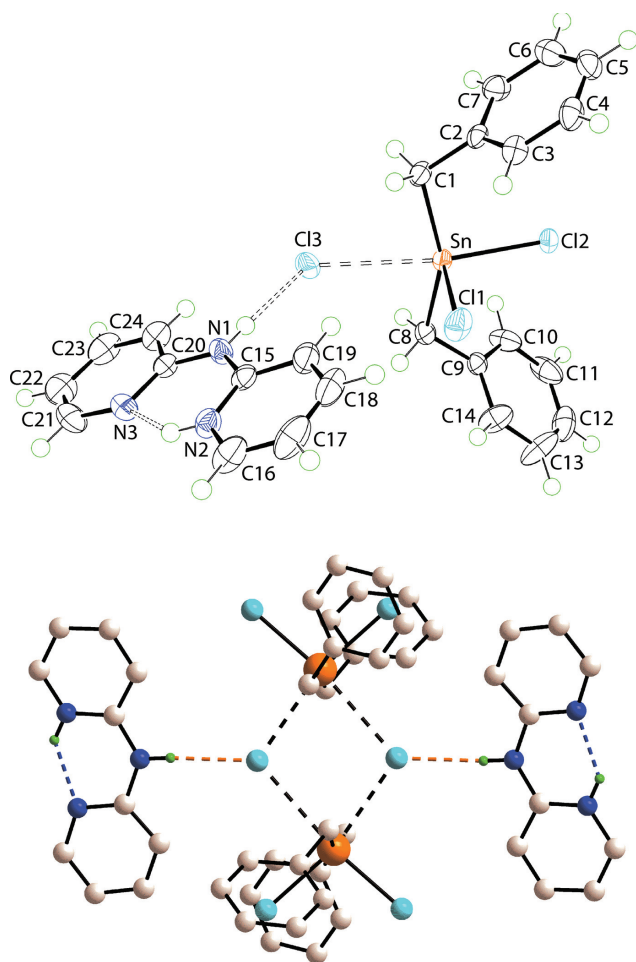


See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink*

Crystal structure of 2-(pyridin-2-ylamino)pyridinium chloride dibenzylidichlorostannane, $[\text{C}_{10}\text{H}_{10}\text{N}_3]\text{Cl}$, $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{Sn}$



Abstract

$\text{C}_{24}\text{H}_{24}\text{Cl}_3\text{N}_3\text{Sn}$, triclinic, $P\bar{1}$ (no. 2), $a = 10.2029(2)$ Å, $b = 10.6071(2)$ Å, $c = 12.1389(3)$ Å, $\alpha = 71.395(2)^\circ$, $\beta = 82.665(2)^\circ$, $\gamma = 73.340(2)^\circ$, $V = 1191.84(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0175$, $wR_{\text{ref}}(F^2) = 0.0447$, $T = 100(2)$ K.

CCDC no.: 2023877

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:	$0.12 \times 0.10 \times 0.04$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	11.7 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	28457, 4247, 0.040
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4094
$N(\text{param})_{\text{refined}}$:	286
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

Dibenzyltin dichloride was synthesised by the direct reaction of benzyl chloride (Merck) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. The dithiocarbamate ligand was prepared in situ from the reaction of CS_2 (Merck 0.25 mmol), 2,2'-dipyridylamine (Sigma-Aldrich, 0.43 g, 0.25 mmol) and potassium hydroxide (0.03 mL; 50% w/v) in methanol solution (15 mL); CS_2 was added dropwise. The resulting mixture was kept at 273 K for 0.5 h. Dibenzyltin dichloride (0.09 g, 0.25 mmol) in methanol (10 mL) was added to the solution of the anticipated potassium 2,2'-dipyridyl dithiocarbamate. The resulting mixture was stirred and refluxed for 2.5 h. The filtrate was evaporated slowly until a white precipitate was formed. The precipitate was washed

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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	0.54835(2)	0.41613(2)	0.70308(2)	0.01496(5)
Cl1	0.43315(5)	0.46505(5)	0.87854(4)	0.02712(11)
Cl2	0.74307(4)	0.23382(4)	0.79596(3)	0.01846(9)
Cl3	0.34518(4)	0.62459(4)	0.53950(4)	0.02362(10)
N1	0.06254(16)	0.80413(16)	0.62034(13)	0.0191(3)
H1N	0.1419(14)	0.761(2)	0.6017(19)	0.023*
N2	−0.07689(17)	0.87462(16)	0.76928(14)	0.0215(3)
H2N	−0.1405(18)	0.907(2)	0.7207(17)	0.026*
N3	−0.16231(17)	0.91301(17)	0.56133(14)	0.0237(3)
C1	0.64245(19)	0.58557(18)	0.64773(15)	0.0184(4)
H1A	0.658998	0.610170	0.562293	0.022*
H1B	0.578318	0.666663	0.666092	0.022*
C2	0.77449(19)	0.55371(17)	0.70400(15)	0.0161(4)
C3	0.7780(2)	0.55626(18)	0.81780(16)	0.0194(4)
H3	0.694749	0.580335	0.860449	0.023*
C4	0.9019(2)	0.5240(2)	0.86914(17)	0.0241(4)
H4	0.902846	0.526969	0.946415	0.029*
C5	1.0244(2)	0.4874(2)	0.80864(18)	0.0263(4)
H5	1.109178	0.464474	0.844344	0.032*
C6	1.0220(2)	0.4846(2)	0.69547(19)	0.0283(4)
H6	1.105407	0.460160	0.653102	0.034*
C7	0.8978(2)	0.5176(2)	0.64414(17)	0.0232(4)
H7	0.897216	0.515343	0.566591	0.028*
C8	0.4188(2)	0.2963(2)	0.68634(16)	0.0206(4)
H8A	0.323305	0.341950	0.705407	0.025*
H8B	0.423156	0.298771	0.603763	0.025*
C9	0.44941(18)	0.14986(18)	0.75868(15)	0.0159(3)
C10	0.5497(2)	0.0498(2)	0.7213(2)	0.0281(4)
H10	0.606098	0.077504	0.654322	0.034*
C11	0.5685(2)	−0.0879(2)	0.7795(2)	0.0345(5)
H11	0.635686	−0.154276	0.751058	0.041*
C12	0.4906(2)	−0.1308(2)	0.8788(2)	0.0332(5)
H12	0.503175	−0.226151	0.918585	0.040*
C13	0.3946(3)	−0.0332(2)	0.91928(18)	0.0383(6)
H13	0.341875	−0.061494	0.988571	0.046*
C14	0.3738(2)	0.1061(2)	0.86001(18)	0.0292(5)
H14	0.307099	0.172071	0.889186	0.035*
C15	0.0461(2)	0.81317(18)	0.73028(16)	0.0186(4)
C16	−0.0993(3)	0.8855(2)	0.87911(17)	0.0307(5)
H16	−0.188040	0.929058	0.903723	0.037*
C17	0.0046(3)	0.8343(2)	0.95371(18)	0.0346(5)
H17	−0.010393	0.841841	1.030483	0.042*
C18	0.1346(2)	0.7700(2)	0.91534(18)	0.0306(5)
H18	0.208277	0.733500	0.966714	0.037*
C19	0.1565(2)	0.7592(2)	0.80492(17)	0.0252(4)
H19	0.244700	0.716063	0.779004	0.030*
C20	−0.03543(19)	0.84710(18)	0.53642(16)	0.0183(4)
C21	−0.2535(2)	0.9557(2)	0.4773(2)	0.0318(5)
H21	−0.344558	1.003260	0.493129	0.038*
C22	−0.2223(2)	0.9343(2)	0.36997(19)	0.0334(5)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H22	−0.289674	0.966956	0.313051	0.040*
C23	−0.0900(2)	0.8639(2)	0.34716(18)	0.0300(5)
H23	−0.065611	0.846313	0.274252	0.036*
C24	0.0056(2)	0.8197(2)	0.43039(17)	0.0250(4)
H24	0.097098	0.771745	0.416306	0.030*

with n-hexane and recrystallised from dimethyl sulfoxide. The title compound was a side-product from the recrystallisation of the product.

Yield: 0.070 g (48.3%). **M. pt** (Stuart SMP30 digital melting point apparatus; uncorrected): 404–406 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm^{−1}): 3023 (w) ν(N–H), 1655 (m) ν(C=C), 1597 (m), 1452 (s) ν(C=N), 1245 (m) ν(C–N), 757 (s) ν(N–H). **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer; chemical shifts relative to Me₄Si, DMSO-*d*₆ solution, ppm): δ 2.97 (s, 4H, –CH₂), 6.86–7.68 (16H, Ph-H, Py-H), 8.22 (s, 2H, Py-H), 9.72 (b, 1H, NH); one NH not observed. **¹³C{¹H} NMR** (as for ¹H NMR): 49.9 (CH₂), 112.3, 116.3, 124.7, 127.6, 127.9, 129.0, 129.4, 129.7, 129.9, 130.2, 138.1, 140.5, 147.6, 154.7 (Ph-C, Py-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) = 1.2*U*_{eq}(C). The N-bound H atoms were refined with N–H = 0.86 ± 0.01 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(N).

Comment

The title salt co-crystal was isolated during the course of structural investigations of organotin dithiocarbamate compounds of general formula R₂Sn[S₂CN(R')R'']Cl [6, 7] motivated by the known biological activity, in particular anti-bacterial and anti-cancer potential, of related organotin dithiocarbamate species [8]. As sometimes happens in this chemistry, reactions generate incomplete species or decomposition products [9]. In the present case, it is apparent the desired (2-pyridyl)₂NCS₂[−] dithiocarbamate anion did not completely form and instead [(2-pyridyl)(2-pyridinium)NH]Cl·(PhCH₂)₂SnCl₂, (I), precipitated in good yield allowing characterisation by spectroscopy as well as by single crystal X-ray crystallography.

The molecular structures of the components comprising the asymmetric unit of (I) are shown in the figure (70% displacement ellipsoids). The pyridinium and pyridyl rings are connected by a charge-assisted pyridinium-N–H⋯N(pyridyl) hydrogen bond [N2–H2n⋯N3: H2n⋯N3 = 1.95(2) Å, N2⋯N3 = 2.646(2) Å with

angle at H2n = 137.4(19)°. As a consequence, the two rings are close to co-planar with the dihedral angle between them being 2.64(10)°. The Sn atom in $(PhCH_2)_2SnCl_2$ of (I) is coordinated by two methylene-C atoms [Sn—C1 & C8 = 2.1581(18) & 2.1451(19) Å] and two chloride atoms [Sn—Cl1 & Cl2 = 2.4297(4) & 2.4363(4) Å]. These bond lengths compare with the Sn—C [2.143(2) Å] and Sn—Cl [2.3695(4) Å] in two-fold symmetric $(PhCH_2)_2SnCl_2$ in the pure crystal [10].

The significant disparity in the Sn—Cl parameters between the two molecules of $(PhCH_2)_2SnCl_2$ is traced to the close association of the Cl3 atoms to the Sn centre in (I). As shown in the lower view of the figure, the constituents of (I) assemble about a centre of inversion to form a six-membered aggregate whereby the two Sn centres are bridged by two Cl3 atoms with Sn—Cl3 and Sn—Cl3ⁱ separations of 2.9581(5) and 3.1246(5) Å, respectively; symmetry operation (i) 1 − x, 1 − y, 1 − z. The ability of diorganotin dichlorides [11] to increase their coordination number by forming intermolecular Sn···Cl secondary bonding interactions [12, 13] is well established in the literature as is the resultant distortion in the coordination geometry about the Sn atom.

The angles about the Sn atom in pure $(PhCH_2)_2SnCl_2$ [10] range from a narrow 99.001(18)° for the Cl—Sn—Cl angle to 136.30(8)° for C—Sn—C. In (I), as a result of the Sn···Cl contacts, the C—Sn—C angle has expanded to 155.24(7)°; the narrowest angle is 95.87(5)° for C8—Sn—Cl1. The connections between the cations and the chloride atoms occur via amine-N—H···Cl hydrogen bonding [N1—H1n···Cl3: H1n···Cl3 = 2.354(19) Å, N1···Cl3 = 3.1979(17) Å with angle at H1n = 171.8(19)°].

In the literature, there are only two structural analogues of the dimeric aggregate observed in (I). These are formulated as $\{[SnCl_3(CH_3)_2]_2\}^{2-}$ and feature shorter Sn—Cl(bridging) distances; each dimer is disposed about a centre of inversion, as in (I). In the salt with an organorhodium counter-cation [14], the Sn—Cl(bridging) bond lengths are 2.759(2) and 2.944(3) Å, and in the example with a Schiff-base-based cation [15], the distances are 2.836(3) and 2.899(4) Å. In (I), where the bridging-Cl atoms form strong hydrogen bonding interactions, the Sn—Cl(bridging) distances are significantly elongated.

In the crystal, the six-membered aggregates are connected into a supramolecular layer in the *ab*-plane by pyridyl-C—H···π(phenyl) [C22—H22···Cg(C9—C14)ⁱⁱ: H22···Cg(C9—C14)ⁱⁱ = 2.51 Å with angle at H22 = 65° for (ii) − x, 1 − y, 1 − z] interactions. Layer stack along the *c*-axis without directional interactions between them.

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