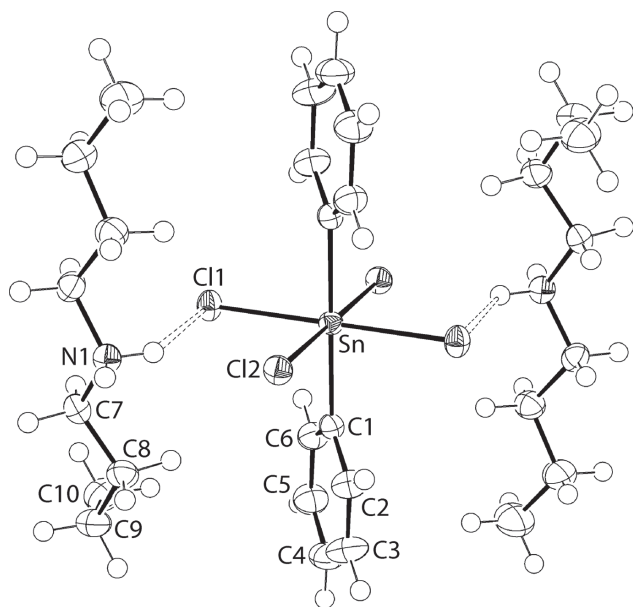


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# Crystal structure of bis(di-*n*-butylammonium) tetrachloridodiphenylstannate(IV), C<sub>28</sub>H<sub>50</sub>Cl<sub>4</sub>N<sub>2</sub>Sn



**Table 1:** Data collection and handling.

Crystal:	Prism, colorless
Size:	0.16 × 0.10 × 0.06 mm
Wavelength:	Cu K $\alpha$ radiation (1.54178Å)
$\mu$ :	9.02 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$ -scans
$\theta_{\max}$ , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	20835, 3025, 0.028
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 2871
$N(\text{param})_{\text{refined}}$ :	168
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX and ORTEP [4]

## Source of material

Carbon disulfide (0.12 mL, 2 mmol) was slowly added to a stirred solution of di-*n*-butylamine (0.34 mL, 2 mmol) in acetone at 273 K. The solution was stirred for 30 min. Next, potassium hydroxide (50% w/v, 0.23 mL) was added dropwise into the solution which was stirred for a further 30 min. Then, diphenyltin dichloride (0.34 g, 1 mmol) in acetone was added into the mixture and stirring was continued for 3 h. The solvent was gradually removed by evaporation until a white solid was obtained. The precipitate was recrystallized from acetone:methanol (1:1) to yield a small number of colourless crystals. The sample was determined crystallographically to be a side-product isolated during the formation of the anticipated dithiocarbamate compound. Yield: 0.020 g (1.5%). **IR** (ATR, cm<sup>-1</sup>) 2975(w)  $\nu$ (N–H), 1636(m)  $\nu$ (C=C), 864(m)  $\nu$ (N–H). **<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) 0.90 (t, 6H, –CH<sub>3</sub>), 1.28–1.37 (m, 4H, –NCH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–), 1.51–1.59 (m, 4H, –NCH<sub>2</sub>–CH<sub>2</sub>–), 2.85–2.89 (m, 4H, –NCH<sub>2</sub>–), 7.28–7.53 (m, 4H, *ortho*–C<sub>6</sub>H<sub>5</sub>), 7.90–8.00 (m, 4H, *meta*–C<sub>6</sub>H<sub>5</sub>), 8.31 (s, 2H, *para*–C<sub>6</sub>H<sub>5</sub>). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) 14.0 (s, –CH<sub>3</sub>), 19.7 (s, –NCH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–), 28.0 (s, –NCH<sub>2</sub>–CH<sub>2</sub>–), 47.0 (s, –NCH<sub>2</sub>–), 127.7 (s, *para*–C<sub>6</sub>H<sub>5</sub>), 128.1 (s, *meta*–C<sub>6</sub>H<sub>5</sub>), 128.3 (s, *ortho*–C<sub>6</sub>H<sub>5</sub>), 135.2 (s, *ipso*–C<sub>6</sub>H<sub>5</sub>).

## Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2–1.5U_{\text{eq}}(\text{C})$ . N-bound H atoms were located in difference Fourier maps and refined subject to distance and  $U_{\text{iso}}(\text{H})$  restraints.

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## Abstract

C<sub>28</sub>H<sub>50</sub>Cl<sub>4</sub>N<sub>2</sub>Sn, monoclinic,  $P2_1/c$  (no. 14),  $a = 12.3981(2)$  Å,  $b = 13.2742(2)$  Å,  $c = 11.0847(2)$  Å,  $\beta = 111.657(2)^\circ$ ,  $V = 1695.49(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{\text{gt}}(F) = 0.0161$ ,  $wR_{\text{ref}}(F^2) = 0.0431$ ,  $T = 100(2)$  K.

**CCDC no.:** 1902634

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	U <sub>iso</sub> <sup>*</sup> /U <sub>eq</sub>
Sn	0.500000	0.500000	0.000000	0.01437(5)
Cl1	0.52108(3)	0.32601(2)	0.10888(3)	0.01906(8)
Cl2	0.49551(3)	0.41841(2)	-0.21255(3)	0.01873(8)
N1	0.51321(10)	0.18136(9)	-0.11260(11)	0.0180(2)
H1N	0.5096(14)	0.2456(7)	-0.0940(15)	0.022*
H2N	0.5064(13)	0.1804(12)	-0.1935(9)	0.022*
C1	0.31423(13)	0.48761(10)	-0.06596(15)	0.0178(3)
C2	0.24451(15)	0.50462(11)	-0.19495(17)	0.0254(4)
H2	0.278751	0.524478	-0.255066	0.030*
C3	0.12476(16)	0.49270(13)	-0.23652(18)	0.0320(4)
H3	0.077824	0.504972	-0.324807	0.038*
C4	0.07339(13)	0.46322(13)	-0.15079(16)	0.0302(4)
H4	-0.008239	0.453883	-0.180092	0.036*
C5	0.14221(13)	0.44738(13)	-0.02151(15)	0.0281(3)
H5	0.107598	0.427899	0.038407	0.034*
C6	0.26179(13)	0.45997(12)	0.02053(14)	0.0233(3)
H6	0.308272	0.449579	0.109395	0.028*
C7	0.41370(12)	0.12705(11)	-0.09800(13)	0.0194(3)
H7A	0.425830	0.122019	-0.004776	0.023*
H7B	0.409498	0.057867	-0.132795	0.023*
C8	0.30038(13)	0.18167(11)	-0.16971(14)	0.0229(3)
H8A	0.288214	0.186237	-0.262976	0.028*
H8B	0.305125	0.251070	-0.135424	0.028*
C9	0.19752(13)	0.12748(13)	-0.15480(15)	0.0283(3)
H9A	0.124719	0.156225	-0.217470	0.034*
H9B	0.200186	0.055437	-0.176623	0.034*
C10	0.19553(14)	0.13552(14)	-0.01895(16)	0.0321(4)
H10A	0.266380	0.105538	0.043489	0.048*
H10B	0.127675	0.099619	-0.015455	0.048*
H10C	0.191237	0.206602	0.002758	0.048*
C11	0.62965(12)	0.14119(11)	-0.03105(14)	0.0211(3)
H11A	0.639205	0.072655	-0.060903	0.025*
H11B	0.635771	0.136474	0.060383	0.025*
C12	0.72486(12)	0.20931(12)	-0.03968(14)	0.0242(3)
H12A	0.711464	0.278870	-0.016153	0.029*
H12B	0.721525	0.210234	-0.130295	0.029*
C13	0.84466(14)	0.17466(13)	0.04961(17)	0.0325(4)
H13A	0.847650	0.172709	0.140076	0.039*
H13B	0.858613	0.105523	0.025185	0.039*
C14	0.93965(15)	0.24399(15)	0.0423(2)	0.0454(5)
H14A	0.939574	0.243365	-0.046131	0.068*
H14B	1.015114	0.220602	0.103093	0.068*
H14C	0.925510	0.312711	0.065254	0.068*

## Discussion

According to a search of the Cambridge Structural Database [5], there are 16 structures featuring the [Ph<sub>2</sub>SnCl<sub>4</sub>]<sup>2-</sup> di-anion. The isolation of these di-anions can be the result of deliberate design, as in the case of the bis(mefloquinium) salt, formed from the reaction of two molar equivalents of mefloquinium chloride and Ph<sub>2</sub>SnCl<sub>2</sub> [6], or adventitious, as for bis(6-methylpyridinium-2-carboxaldehyde phenylhydrazone)

salt, formed during an attempt to prepare a coordination compound [7]. The present study is an example of the adventitious generation of the di-anion, being isolated as its bis(di-*n*-butylammonium) salt in an unsuccessful attempt to form a diphenyltin bis(dithiocarbamate) compound, see *Source of material*.

The asymmetric unit of [(*n*-butyl)<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[Ph<sub>2</sub>SnCl<sub>4</sub>] comprises a cation in a general position and the di-anion with the tin atom situated on a crystallographic centre of inversion as shown in the Figure (70% displacement ellipsoids with unlabelled atoms related by the symmetry operation *i*: 1 - *x*, 1 - *y*, - *z*). From symmetry, the donor set is *trans*-C<sub>2</sub>Cl<sub>4</sub>, which is the universally adopted structural motif for these di-anions [5]. At 2.5742(3) and 2.5750(3) Å, respectively, the independent Sn-Cl1 and Sn-Cl2 bond lengths are equal within experimental error. Among the literature precedents, the Sn-Cl bond lengths range from a short 2.4966(6) Å to a long 2.6723(5) Å, and these extreme values are found in the bis(8-(methylamino)quinolinium) salt wherein the tin atom lies on a crystallographic 2-fold axis of symmetry [8].

The most prominent feature of the molecular packing is the formation of charge-assisted ammonium-N-H...Cl hydrogen bonds. The ammonium-N-H1n atom is bifurcated, forming N-H...Cl hydrogen bonds with each of the Cl1 and Cl2 atoms derived from one di-anion to form a S(4) loop [N1-H1n...Cl1: H1n...Cl1 = 2.446(15) Å, N1...Cl1 = 3.0898(12) Å with angle at H1n = 130.2(12)° and N1-H1n...Cl2: H1n...Cl2 = 2.617(11) Å, N1...Cl2 = 3.3163(12) Å with angle at H1n = 136.8(13)°]. In this manner and from symmetry, three-molecule aggregates are formed. These are connected into a supramolecular layer in the *bc*-plane by N1-H2n...Cl1 hydrogen bonds [N1-H2n...Cl1<sup>ii</sup>: H2n...Cl1<sup>ii</sup> = 2.266(11) Å, N1...Cl1<sup>ii</sup> = 3.1262(12) Å with angle at H2n = 170.5(15)° for symmetry operation *ii*: *x*, 1/2 - *y*, -1/2 + *z*]. The layers thus formed stack along the *a* axis without directional interactions between them.

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