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

Crystal structure of bis(di-*n*-butylammonium) tetrachloridodiphenylstannate(IV), C₂₈H₅₀Cl₄N₂Sn

Table 1: Data collection and handling.

Crystal:	Prism, colorless
Size:	0.16 × 0.10 × 0.06 mm
Wavelength:	Cu K α radiation (1.54178 Å)
μ :	9.02 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω -scans
$\theta_{\max}$, completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	20835, 3025, 0.028
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2871
$N(\text{param})_{\text{refined}}$:	168
Programs:	CrysAlis ^{PRO} [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⁻¹) 2975(w) ν (N–H), 1636(m) ν (C=C), 864(m) ν (N–H). **¹H NMR** (400 MHz, DMSO-*d*₆) 0.90 (t, 6H, –CH₃), 1.28–1.37 (m, 4H, –NCH₂–CH₂–CH₂–), 1.51–1.59 (m, 4H, –NCH₂–CH₂–), 2.85–2.89 (m, 4H, –NCH₂–), 7.28–7.53 (m, 4H, *ortho*–C₆H₅), 7.90–8.00 (m, 4H, *meta*–C₆H₅), 8.31 (s, 2H, *para*–C₆H₅). **¹³C NMR** (100 MHz, DMSO-*d*₆) 14.0 (s, –CH₃), 19.7 (s, –NCH₂–CH₂–CH₂–), 28.0 (s, –NCH₂–CH₂–), 47.0 (s, –NCH₂–), 127.7 (s, *para*–C₆H₅), 128.1 (s, *meta*–C₆H₅), 128.3 (s, *ortho*–C₆H₅), 135.2 (s, *ipso*–C₆H₅).

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.

<https://doi.org/10.1515/ncrs-2019-0107>

Received February 12, 2019; accepted March 12, 2019; available online June 6, 2019

Abstract

C₂₈H₅₀Cl₄N₂Sn, monoclinic, $P2_1/c$ (no. 14), $a = 12.3981(2)$ Å, $b = 13.2742(2)$ Å, $c = 11.0847(2)$ Å, $\beta = 111.657(2)^\circ$, $V = 1695.49(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0161$, $wR_{\text{ref}}(F^2) = 0.0431$, $T = 100(2)$ 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.

*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

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

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

Atom	x	y	z	U_{iso}^*/U_{eq}
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 [Ph₂SnCl₄]^{2−} 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 Ph₂SnCl₂ [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 adventurous 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)₂NH₂]₂[Ph₂SnCl₄] 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*—C₂Cl₄, 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...Clⁱⁱ: H2n...Clⁱⁱ = 2.266(11) Å, N1...Clⁱⁱ = 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.

Acknowledgements: Sunway University is thanked for support of studies in organotin chemistry.

References

- Agilent Technologies: CrysAlis PRO. Agilent Technologies, Santa Clara, CA, USA (2017).
- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
- Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
- Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **45** (2012) 849–854.
- Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C.: The Cambridge Structural Database. *Acta Cryst.* **B72** (2016) 171–179.

6. Wardell, J. L.; Wardell, S. M. S. V.; Tiekink, E. R. T.; de Lima, G. M.: Bis(2-[[2,8-bis(trifluoromethyl)quinolin-4-yl](hydroxymethyl)piperidin-1-ium) tetrachlorodiphenylstannate(IV). *Acta Crystallogr.* **E66** (2010) m336–m338.
7. Teo, S.-B.; Teo, H.-S.; Yeow, L.-M.; Chang, S.-T.; Teoh, S.-G.; Tiekink, E. R. T.: Protonated ligand outer-sphere complex formed in the reaction of 6-methylpyridine-2-carboxaldehyde phenylhydrazone with Ph_2SnCl_2 . A true case of hydrogen bonding involving an Sn—Cl bond. *J. Coord. Chem.* **49** (2000) 261–268.
8. Hazell, A.; Khoo, L. E.; Ouyang, J.; Rausch, B. J.; Tavares, Z. M.: 8-Methylaminoquinolinium salts of tetrachlorodimethylstannate(IV) and tetrachlorodiphenylstannate(IV). *Acta Crystallogr.* **C54** (1998) 728–732.