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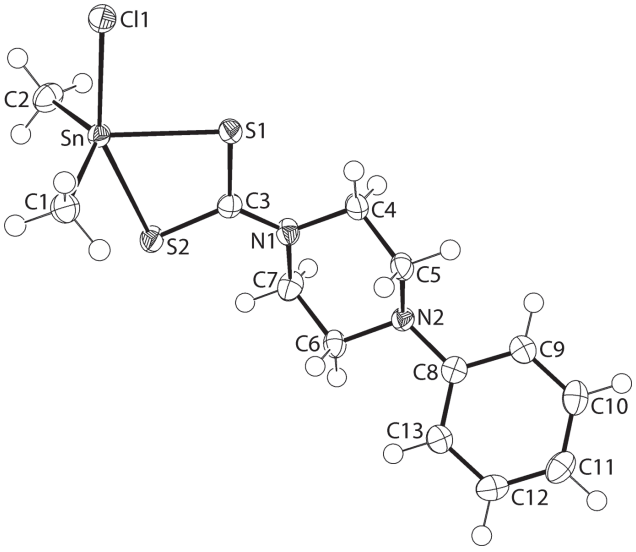
Crystal structure of chlorido-dimethyl-(phenylpiperazine-1-carbodithioato-κ^2 *S*,*S*′)tin(IV), $C_{13}H_{19}ClN_2S_2Sn$



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Abstract

$C_{13}H_{19}ClN_2S_2Sn$, triclinic, $P\bar{1}$ (no. 2), $a = 6.5837(2)$ Å, $b = 9.9458(2)$ Å, $c = 12.8720(3)$ Å, $\alpha = 85.344(2)°$, $\beta = 79.508(2)°$, $\gamma = 83.832(2)°$, $V = 822.33(4)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0176$, $wR_{ref}(F^2) = 0.0461$, $T = 100$ 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.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.13 × 0.04 × 0.03 mm
Wavelength:	Cu *Kα* radiation (1.54178 Å)
μ:	16.1 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	19541, 2930, 0.036
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2870
$N(param)_{refined}$:	174
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined using a Mel-temp II digital melting point apparatus and was uncorrected. The solid-state IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer from 4000 to 400 cm^{-1}. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at room temperature in $CDCl_3$ solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

The dithiocarbamate ligand was prepared in situ (methanol) from the reaction of CS_2 (Merck 0.25 mmol) with 1-phenylpiperazine (Merck, 0.25 mmol) and NaOH (0.02 mL; 50% *w/v*); CS_2 was added dropwise into the methanolic solution (10 mL). The resulting mixture solution was kept at 273 K for 0.5 h. Dimethyltin dichloride (Merck, 0.25 mmol, 0.05 g) in methanol (10 mL) was added to the prepared sodium 1-phenylpiperazinedithiocarbamate. The resulting mixture was stirred under reflux for 2 h. The filtrate was evaporated slowly until a white precipitate was formed. The precipitate was recrystallized from methanol by slow evaporation to yield colourless crystals.

Yield: 0.052 g (49.3%). **M.pt:** 479–480 K. IR (cm^{-1}) 1598 (m) ν(CN), 1216 (m) ν(CS), 1012 (s) ν(CN), 558 (m) ν(SnS). **^{1}H NMR** ($CDCl_3$, ppm): 1.39 (6H, Sn—CH_3), 3.21–3.25 (m, 4H, N—CH_2), 4.17–4.22 (m, 4H, N—CH_2), 6.83–7.23 (m, 5H, Ph—H). **^{13}C NMR** ($CDCl_3$, ppm): 15.6 (Sn—CH_3), 48.9, 50.9 (piperazine-C), 118.1, 125.5, 130.8, 150.4 (Ph—C), 199.9 (CS_2).

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn	0.48439(2)	0.81316(2)	0.39082(2)	0.01348(6)
S1	0.30756(7)	0.60263(5)	0.42166(4)	0.01538(11)
S2	0.58283(7)	0.65990(5)	0.21741(4)	0.01759(11)
Cl1	0.34240(8)	0.85991(5)	0.57712(4)	0.02212(12)
N1	0.3630(3)	0.44530(17)	0.25898(14)	0.0163(4)
N2	0.1508(2)	0.27759(17)	0.15351(14)	0.0148(3)
C1	0.3015(3)	0.9652(2)	0.31460(18)	0.0197(4)
H1A	0.3901	1.0331	0.2768	0.030*
H1B	0.1941	1.0088	0.3676	0.030*
H1C	0.2359	0.9240	0.2641	0.030*
C2	0.8031(3)	0.7907(2)	0.40266(18)	0.0222(5)
H2A	0.8852	0.8210	0.3351	0.033*
H2B	0.8460	0.6952	0.4196	0.033*
H2C	0.8256	0.8454	0.4588	0.033*
C3	0.4135(3)	0.5569(2)	0.29355(17)	0.0149(4)
C4	0.2111(3)	0.3575(2)	0.32026(17)	0.0194(4)
H4A	0.1415	0.4007	0.3857	0.023*
H4B	0.2832	0.2695	0.3408	0.023*
C5	0.0505(3)	0.3345(2)	0.25377(17)	0.0181(4)
H5A	−0.0469	0.2717	0.2937	0.022*
H5B	−0.0302	0.4217	0.2391	0.022*
C6	0.2938(3)	0.3696(2)	0.09272(17)	0.0167(4)
H6A	0.2164	0.4572	0.0760	0.020*
H6B	0.3606	0.3303	0.0252	0.020*
C7	0.4592(3)	0.3926(2)	0.15655(18)	0.0196(4)
H7A	0.5439	0.3061	0.1682	0.023*
H7B	0.5523	0.4579	0.1164	0.023*
C8	0.0112(3)	0.2269(2)	0.09669(17)	0.0153(4)
C9	−0.1010(3)	0.1189(2)	0.14391(17)	0.0174(4)
H9	−0.0852	0.0827	0.2129	0.021*
C10	−0.2348(3)	0.0646(2)	0.09047(19)	0.0212(5)
H10	−0.3096	−0.0087	0.1231	0.025*
C11	−0.2603(3)	0.1165(2)	−0.01024(18)	0.0225(5)
H11	−0.3528	0.0794	−0.0464	0.027*
C12	−0.1495(3)	0.2228(2)	−0.05748(18)	0.0216(5)
H12	−0.1660	0.2586	−0.1265	0.026*
C13	−0.0139(3)	0.2779(2)	−0.00447(17)	0.0180(4)
H13	0.0617	0.3506	−0.0377	0.022*

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) = 1.2–1.5U_{eq}(C).

Comment

Recently, the structure of the dithiocarbamate ligand featured in the title compound, $Me_2Sn[S_2CN(CH_2CH_2)_2NPh]Cl$, became available in its salt with the 4-phenylpiperazin-1-ium cation [5]. Organotin dithiocarbamate compounds are well-known as potential pharmaceuticals and as having applications as synthetic precursors for the chemical vapour deposition of tin sulphide nanomaterials [6]. It was biological considerations [7] that led to the formation and crystallographic analysis of the title compound.

The molecular structure of $Me_2Sn[S_2CN(CH_2CH_2)_2NPh]Cl$ is shown in the figure (70% displacement ellipsoids) and comprises a penta-coordinate tin atom. The dithiocarbamate ligand is asymmetrically chelating the tin centre, forming Sn—S1, S2 bond lengths of 2.4734(5) and 2.7458(5) Å, respectively. The longer Sn—S2 bond is partly due to the approximately trans disposition of the S2 atom to the chloride, i.e. S2—Sn—Cl1 = 155.971(16)°. The difference in the Sn—S separations, i.e. Δ(Sn—S) = [(Sn—S_{long}) − (Sn—S_{short})] = 0.27 Å, results in a disparity in the associated C—S bond lengths. Thus, the C3—S1 bond length [1.746(2) Å] associated with the more tightly bound sulphur atom is longer than the equivalent bond [1.714(2) Å] involving the less tightly bound S2 atom. This contrasts the situation in the structure of the salt of the dithiocarbamate anion [5] whereby the C1—S1, S2 bond lengths of 1.7192(14) and 1.7249(14) Å, respectively, are experimentally equivalent. The Sn—Cl1 bond length is 2.4722(5) Å. A quantitative measure of a five-coordinate geometry is τ, which ranges from 0.0 to 1.0 for ideal square-pyramidal and trigonal-bipyramidal coordination geometries, respectively [8]. The value of τ computes to 0.40 in the title compound, indicating a highly distorted geometry. The distortion is ascribed in part to the acute chelate S1—Sn—S2 angle of 68.887(16)° as well as the wide angle subtended by the tin-bound methyl groups, with C1—Sn—C2 = 132.18(9)°. In summary, the structure of $Me_2Sn[S_2CN(CH_2CH_2)_2NPh]Cl$ conforms to the expected motif for compounds of this type [6, 9, 10].

There are several non-covalent interactions less than the sum of the respective van der Waals radii in the molecular packing. Thus, methylene-C—H···Cl interactions lead to the formation of centrosymmetric dimeric aggregates [C5—H5a···Cl1^i: H5a···Cl1^i = 2.70 Å, C5···Cl1^i = 3.676(2) Å with angle at H5a = 170° for symmetry operation (i) −x, 1 − y, 1 − z]. These aggregates are connected into a supramolecular layer with a flat topology and parallel to (0 1 −1). The layer is sustained by C—H···π(phenyl) and π—π stacking interactions involving the same phenyl ring [C7—H7a···Cg(C8—C13)^{ii}: H7a···Cg(C8—C13)^{ii} = 2.76 Å, C7···Cg(C8—C13)^{ii} = 3.500(2) Å with angle at H7a = 132° and Cg(C8—C13)···Cg(C8—C13)^{iii} = 3.7795(12) Å for (ii) 1 + x, y, z and (iii) −x, −y, −z]. Weak phenyl-C—H···S(thione) interactions [C13—H13···S2^{iv}: H13···S2^{iv} = 2.98 Å, C13···S2^{iv} = 2.9774(19) Å with angle at H13 = 128° for (iv) 1 − x, 1 − y, −z] feature in the inter-layer region.

In order to analyse the molecular further, the Hirshfeld surfaces were calculated along with the full and delineated two-dimensional fingerprint plots using Crystal Explorer [11] and established protocols [12]. The aforementioned phenyl-C—H···S(thione) interaction is the only one less than the sum of the van der Waals radii of sulphur and hydrogen in the crystal, with other H···S contacts occurring at longer

distances. Overall, S···H/H···S contacts contribute 13.3% of all contacts on the calculated Hirshfeld. Other significant surface contacts are of the type Cl···H/H···Cl (13.2%) and C···H/H···C (11.1%). However, none of these compare in significance to H···H contacts, with these making the greatest percentage contribution of 56.4% of all contacts.

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References

1. Rigaku Oxford Diffraction: CrysAlis^{PRO}. Rigaku Corporation, Oxford, UK (2018).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
5. Lo, K. M.; Lee, S. M.; Tiekink, E. R. T.: Crystal structure of 4-phenylpiperazin-1-ium (4-phenylpiperazin-1-yl) carbothioylsulfanide, $[C_{10}H_{15}N_2][C_{11}H_{13}N_2S_2]$. Z. Kristallogr. NCS **234** (2019). DOI: 10.1515/ncrs-2019-0512.
6. Tiekink, E. R. T.: Tin dithiocarbamates: applications and structures. Appl. Organomet. Chem. **22** (2008) 533–550.
7. Anasamy, T.; Thy, C. K.; Lo, K. M.; Chee, C. F.; Yeap, S. K.; Kamalidehghan, B.; Chung, Lip, Y.: Tribenzyltin carboxylates as anticancer drug candidates: effect on the cytotoxicity, motility and invasivenessof breast cancer cell lines. Eur. J. Med. Chem. **125** (2017) 770–783.
8. Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C.: Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen–sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(*N*-methylbenzimidazol-2′-yl)-2,6-dithiaheptane]- copper(II) perchlorate. J. Chem. Soc., Dalton Trans. (1984) 1349–1356. https://pubs.rsc.org/en/content/articlelanding/1984/dt/dt9840001349#!divAbstract.
9. Tiekink, E. R. T.; Hall, V. J.; Buntine, M. A.: An examination of the influence of crystal structure on molecular structure. The crystal and molecular structures of some diorganotinchloro-(*N*,*N*-dialkyldithiocarbamate)s, $R_2Sn(S_2CNR'_2)Cl$, R = Me, tBu, Ph, Cy; $R'_2 = (Et)_2$, (Et, Cy) and $(Cy)_2$: a comparison between solid state and theoretical structures. Z. Kristallogr. Cryst. Mater. **214** (1999) 124–134.
10. Zia-ur-Rehman; Barsan, M. M.; Wharf, I.; Muhammad, N.; Ali, S.; Meetsma, A.; Butler, I. S.: Synthesis, spectroscopic characterization, and crystal structures of two chlorodiorganotin(IV) 4-(2-methoxyphenyl)piperazine-1-carbodithioates. Inorg. Chim. Acta **361** (2008) 3322–3326.
11. Turner, M. J.; Mckinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A.: Crystal Explorer v17. The University of Western Australia, Australia (2017).
12. Tan, S. L.; Jotani, M. M.; Tiekink, E. R. T.: Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. Acta Crystallogr. **E75** (2019) 308–318.