

## Dichloridodiphenylbis(thiourea- $\kappa$ S)-tin(IV)

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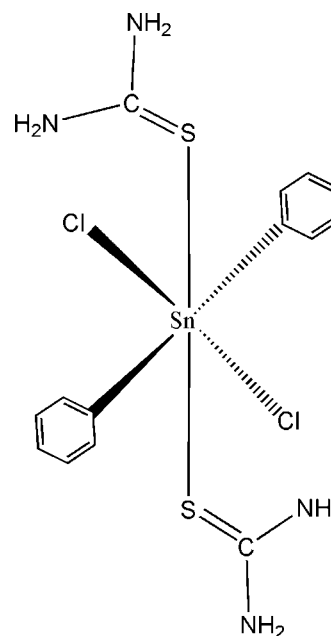
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Key indicators: single-crystal X-ray study;  $T = 150$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.019;  $wR$  factor = 0.051; data-to-parameter ratio = 17.7.

The title compound,  $[\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2(\text{CH}_4\text{N}_2\text{S})_2]$ , has been obtained from the reaction between  $\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2$  and  $\text{SC}(\text{NH}_2)_2$ . The asymmetric unit consists of one half of the molecular unit, the remainder generated by a twofold rotation axis located along the  $\text{Cl}-\text{Sn}-\text{Cl}$  bonds. The  $\text{Sn}^{\text{IV}}$  atom is coordinated by two phenyl groups, two Cl atoms and two thiourea ligands in an all *trans* octahedral  $\text{C}_2\text{Cl}_2\text{S}_2$  environment. Individual molecules are connected through  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen bonds, leading to a three-dimensional network structure. Intramolecular  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen bonds are also present.

### Related literature

For background to organotin(IV) chemistry, see: Kapoor *et al.* (2005); Sadiq-ur-Rehman *et al.* (2007); Zhang *et al.* (2006). For organotin(IV) compounds exhibiting biological activity, see: Nath *et al.* (2001); Pellerito & Nagy (2002). For chlorido-tin(IV) complexes, see: Amini *et al.* (2002); Müller *et al.* (2008). For tin(IV) complexes containing thiourea groups, see: Donaldson *et al.* (1984); Sow *et al.* (2012); Wirth *et al.* (1998).



### Experimental

#### Crystal data

$[\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2(\text{CH}_4\text{N}_2\text{S})_2]$   
 $M_r = 496.03$   
 Tetragonal,  $I4_1/a$   
 $a = 14.6401$  (2) Å  
 $c = 17.7899$  (3) Å  
 $V = 3812.95$  (10) Å<sup>3</sup>

$Z = 8$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.84$  mm<sup>-1</sup>  
 $T = 150$  K  
 $0.35 \times 0.35 \times 0.25$  mm

#### Data collection

Nonius KappaCCD diffractometer  
 Absorption correction: multi-scan  
 (SORTAV; Blessing, 1995)  
 $T_{\text{min}} = 0.565$ ,  $T_{\text{max}} = 0.656$

23870 measured reflections  
 2183 independent reflections  
 1892 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.041$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$   
 $wR(F^2) = 0.051$   
 $S = 1.06$   
 2183 reflections  
 123 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.72$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1B}\cdots\text{Cl2}$	0.86 (3)	2.50 (3)	3.345 (2)	166 (2)
$\text{N2}-\text{H2A}\cdots\text{Cl1}^{\dagger}$	0.81 (3)	2.41 (3)	3.2119 (19)	170 (3)

Symmetry code: (i)  $-y + \frac{3}{4}, x + \frac{1}{4}, z + \frac{1}{4}$ .

Data collection: COLLECT (Nonius, 1999); cell refinement: DENZO and SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO and SCALEPACK; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: WinGX (Farrugia, 2012).

We thank Dr Raymundo Cea Olivares, Instituto de Química UNAM, Mexico, for performing the elemental analyses.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2764).

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## supporting information

*Acta Cryst.* (2013). E69, m539–m540 [doi:10.1107/S1600536813024343]

## Dichloridodiphenylbis(thiourea- $\kappa$ S)tin(IV)

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### S1. Comment

Many  $\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2$  adducts have previously been reported and structurally characterized (Kapoor *et al.*, 2005; Müller *et al.*, 2008; Sadiq-ur-Rehman *et al.*, 2007; Sow *et al.*, 2012; Zhang *et al.*, 2006). Organotin (IV) compounds exhibiting biological (e.g antitumour) activity have also been reported (Nath *et al.*, 2001; Pellerito & Nagy, 2002). On allowing  $\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2$  and  $\text{SC}(\text{NH}_2)_2$  to react, crystals of the title compound,  $[\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2(\text{CH}_4\text{N}_2\text{S})_2]$ , (I), were obtained and the structure determined.

The molecule in the structure of compound (I) is located on a twofold rotation axis. The  $\text{Sn}^{\text{IV}}$  atom has an octahedral *trans, trans, trans*- $\text{C}_2\text{S}_2\text{Cl}_2$  coordination sphere (Fig. 1), defined by two carbon atoms of symmetry-related phenyl groups [2.1622 (17) Å], two Cl [2.5194 (6), 2.6224 (6) Å] and two sulfur atoms of the thiourea ligands [2.6755 (4) Å]. The Sn—S bond is somewhat shorter than the analogous bond [2.6945 (7) Å] in the related structure of  $[\text{Sn}_2(\text{C}_2\text{O}_4)(\text{C}_6\text{H}_5)_6(\text{CH}_4\text{N}_2\text{S})_2]$  (Sow *et al.*, 2012), but is in the range of other Sn—S bonds reported for tin(IV) structures containing thiourea ligands (Donaldson *et al.*, 1984; Wirth *et al.*, 1998).

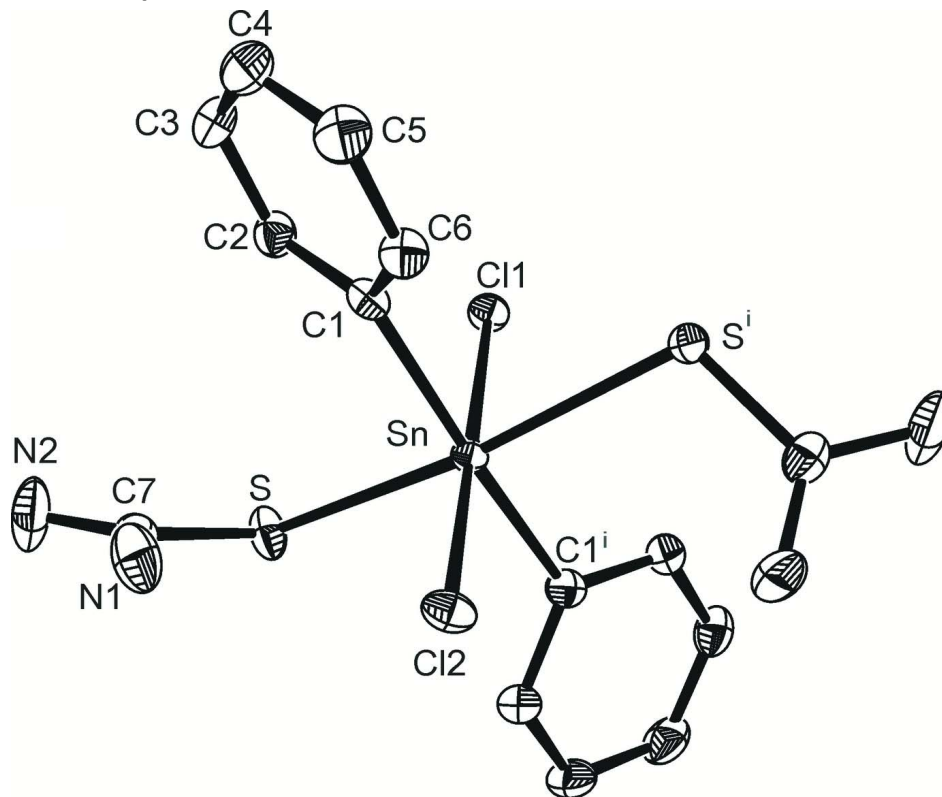
The Sn—Cl2 distance [2.5194 (6) Å] is shorter than the Sn—Cl1 distance [2.6224 (6) Å] as a consequence of the involvement of Cl1 in strong intermolecular  $\text{N2—H2A}\cdots\text{Cl1}$  hydrogen bond formation (Table 1), which leads to the formation of a three-dimensional network structure. Somewhat weaker intramolecular  $\text{N1—H1B}\cdots\text{Cl2}$  hydrogen bonds are also present (Fig. 2). When compared to the unique Sn—Cl distance in  $\{[(\text{CH}_3)_3\text{C}]_2(\text{CH}_3\text{PO})_2\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2\}$  [2.5567 (16) Å] (Müller *et al.*, 2008) or the two Sn—Cl distances in {18-crown-6- $\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$ } [2.5521 (7), 2.5627 (7) Å] (Amini *et al.*, 2002), two adducts in which the Cl atoms are not involved in hydrogen bonding, it appears that in (I) the intermolecular hydrogen bonding has led to a weakened Sn—Cl1 bond and a concomitant strengthening of Sn—Cl2. Moreover, the strength of Sn—Cl2 in comparison with examples of other Sn—Cl bonds where the halogen is not involved in hydrogen bonding suggests that the intramolecular hydrogen bonds are weaker than suggested by their interatomic separation.

### S2. Experimental

All chemicals were purchased from Aldrich (Germany) and used without any further purification. The title compound,  $[\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2(\text{CH}_4\text{N}_2\text{S})_2]$ , has been synthesized from the reaction between  $\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2$  (0.250 g, 0.727 mmol) and  $\text{SC}(\text{NH}_2)_2$  (0.111 g, 1.454 mmol) in a 1:2 ratio in absolute ethanol solution. After stirring for two hours, a clear solution was obtained that was slowly evaporated at room temperature yielding colourless crystals (weight, yield 69%) with a melting point of 515 K. Analytical data for  $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{N}_4\text{S}_2\text{Sn}$  (found) %C: 33.90 (33.87); %H: 3.66 (3.63); %N: 11.29(11.27); %S: 12.93 (12.90); %Sn: 23.93 (23.98).

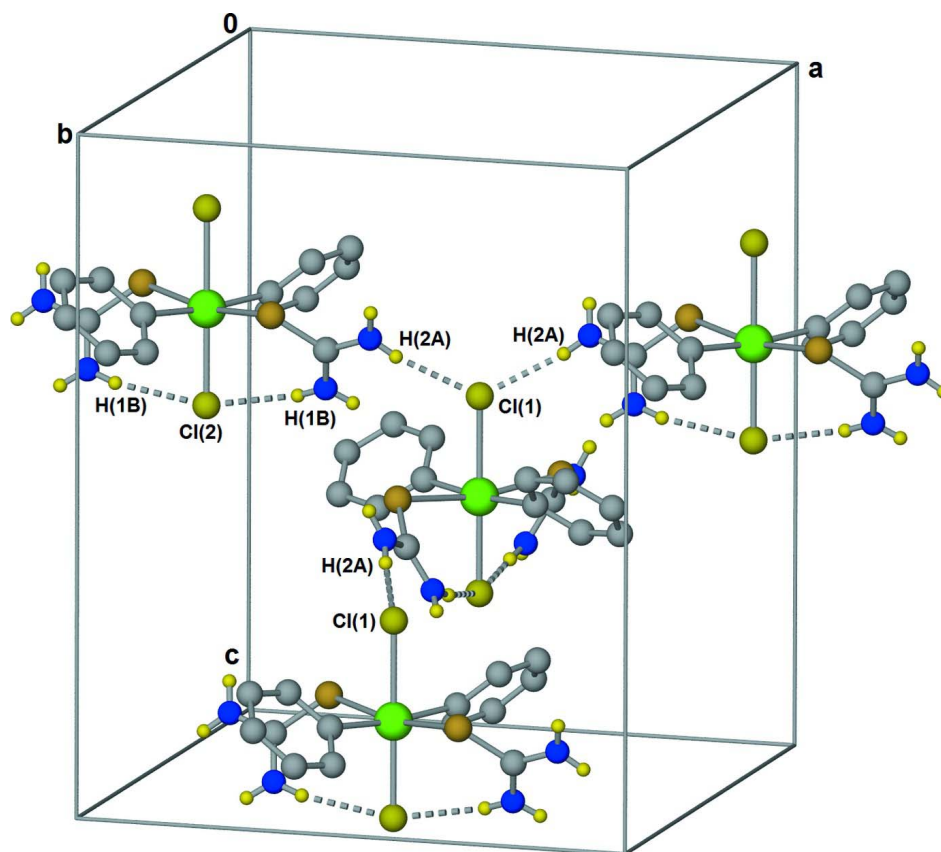
### S3. Refinement

Hydrogen atoms bonded to the N atom have been located in difference Fourier maps and have been freely refined. The other hydrogen atoms have been placed onto calculated position and refined using a riding model, with C—H distances of 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .



**Figure 1**

The molecular structure of (I) showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level; H atoms were omitted for clarity. [Symmetry code i)  $-x, 1/2 - y, z$ .]

**Figure 2**

A section of the lattice structure of (I) showing both the intermolecular N(2)—H(2A)···Cl(1) and intramolecular N(1)—H(1B)···Cl(2) hydrogen bonding interactions as dashed lines. Only selected hydrogen atoms have been included for clarity.

### Dichloridodiphenylbis(thiourea- $\kappa$ S)tin(IV)

#### Crystal data

[Sn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>(CH<sub>4</sub>N<sub>2</sub>S)<sub>2</sub>]

$M_r = 496.03$

Tetragonal,  $I4_1/a$

Hall symbol:  $-I\ 4ad$

$a = 14.6401(2)\ \text{\AA}$

$c = 17.7899(3)\ \text{\AA}$

$V = 3812.95(10)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1968$

$D_x = 1.728\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 13789 reflections

$\theta = 2.9\text{--}27.5^\circ$

$\mu = 1.84\ \text{mm}^{-1}$

$T = 150\ \text{K}$

Block, colourless

$0.35 \times 0.35 \times 0.25\ \text{mm}$

#### Data collection

Nonius KappaCCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

152 2.0 degree images with  $\omega$  scans

Absorption correction: multi-scan  
(*SORTAV*; Blessing, 1995)

$T_{\min} = 0.565$ ,  $T_{\max} = 0.656$

23870 measured reflections

2183 independent reflections

1892 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$   
 $\theta_{\text{max}} = 27.5^\circ$ ,  $\theta_{\text{min}} = 3.3^\circ$   
 $h = -18 \rightarrow 18$

$k = -18 \rightarrow 18$   
 $l = -23 \rightarrow 23$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.019$   
 $wR(F^2) = 0.051$   
 $S = 1.06$   
 2183 reflections  
 123 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods  
 Secondary atom site location: difference Fourier  
 map

Hydrogen site location: inferred from  
 neighbouring sites  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0219P)^2 + 4.1509P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.40 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.72 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97* (Sheldrick,  
 2008),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.00076 (6)

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Sn	0.0000	0.2500	0.371721 (7)	0.01479 (8)
Cl1	0.0000	0.2500	0.22431 (3)	0.01928 (13)
Cl2	0.0000	0.2500	0.51334 (3)	0.02256 (13)
S	0.15011 (3)	0.35281 (3)	0.35755 (3)	0.02464 (11)
N1	0.22306 (14)	0.26557 (13)	0.47461 (10)	0.0378 (4)
H1A	0.2663 (18)	0.2448 (17)	0.4972 (14)	0.054 (8)*
H1B	0.1685 (19)	0.2538 (17)	0.4898 (14)	0.052 (7)*
N2	0.32157 (12)	0.32246 (17)	0.38782 (12)	0.0463 (5)
H2A	0.3644 (18)	0.3077 (18)	0.4143 (15)	0.056 (7)*
H2B	0.331 (2)	0.348 (2)	0.3459 (19)	0.076 (10)*
C1	0.07672 (12)	0.12407 (11)	0.36491 (8)	0.0191 (3)
C2	0.15058 (11)	0.11573 (11)	0.31618 (9)	0.0220 (3)
H2	0.1712	0.1675	0.2888	0.026*
C3	0.19442 (12)	0.03197 (13)	0.30729 (10)	0.0287 (4)
H3	0.2448	0.0266	0.2739	0.034*
C4	0.16417 (13)	-0.04356 (13)	0.34738 (11)	0.0325 (4)
H4	0.1930	-0.1011	0.3406	0.039*
C5	0.09216 (13)	-0.03516 (12)	0.39710 (11)	0.0303 (4)
H5	0.0724	-0.0867	0.4252	0.036*
C6	0.04852 (11)	0.04849 (11)	0.40608 (9)	0.0231 (3)

H6	-0.0008	0.0540	0.4405	0.028*
C7	0.23733 (12)	0.30925 (11)	0.41088 (10)	0.0247 (4)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Sn	0.01624 (10)	0.01267 (10)	0.01545 (10)	-0.00079 (5)	0.000	0.000
Cl1	0.0222 (3)	0.0212 (3)	0.0144 (2)	-0.00041 (19)	0.000	0.000
Cl2	0.0323 (3)	0.0204 (3)	0.0150 (3)	-0.0046 (2)	0.000	0.000
S	0.0184 (2)	0.0218 (2)	0.0337 (2)	-0.00452 (16)	-0.00682 (17)	0.00877 (17)
N1	0.0324 (10)	0.0431 (10)	0.0380 (9)	-0.0012 (8)	-0.0151 (8)	0.0110 (8)
N2	0.0187 (9)	0.0828 (16)	0.0373 (10)	0.0101 (9)	-0.0039 (8)	0.0048 (10)
C1	0.0211 (8)	0.0180 (8)	0.0183 (7)	-0.0031 (6)	-0.0033 (6)	-0.0004 (6)
C2	0.0198 (8)	0.0217 (8)	0.0246 (8)	-0.0008 (6)	0.0003 (6)	0.0015 (6)
C3	0.0201 (9)	0.0310 (10)	0.0352 (10)	0.0061 (7)	0.0019 (7)	-0.0032 (7)
C4	0.0295 (10)	0.0244 (9)	0.0437 (11)	0.0092 (7)	-0.0056 (8)	0.0005 (8)
C5	0.0331 (10)	0.0210 (9)	0.0368 (9)	0.0020 (7)	-0.0030 (8)	0.0084 (7)
C6	0.0246 (8)	0.0216 (8)	0.0231 (8)	0.0003 (6)	-0.0003 (6)	0.0036 (6)
C7	0.0238 (8)	0.0231 (8)	0.0271 (9)	0.0021 (6)	-0.0058 (7)	-0.0057 (7)

*Geometric parameters (Å, °)*

Sn—C1	2.1622 (17)	N2—H2B	0.85 (3)
Sn—C1 <sup>i</sup>	2.1622 (17)	C1—C6	1.390 (2)
Sn—Cl2	2.5194 (6)	C1—C2	1.391 (2)
Sn—Cl1	2.6224 (6)	C2—C3	1.393 (2)
Sn—S <sup>i</sup>	2.6755 (4)	C2—H2	0.9500
Sn—S	2.6755 (4)	C3—C4	1.388 (3)
S—C7	1.7137 (17)	C3—H3	0.9500
N1—C7	1.318 (2)	C4—C5	1.382 (3)
N1—H1A	0.81 (3)	C4—H4	0.9500
N1—H1B	0.86 (3)	C5—C6	1.391 (2)
N2—C7	1.314 (2)	C5—H5	0.9500
N2—H2A	0.81 (3)	C6—H6	0.9500
C1—Sn—C1 <sup>i</sup>	173.57 (8)	C6—C1—C2	119.30 (16)
C1—Sn—Cl2	93.21 (4)	C6—C1—Sn	119.67 (12)
C1 <sup>i</sup> —Sn—Cl2	93.21 (4)	C2—C1—Sn	120.90 (12)
C1—Sn—Cl1	86.79 (4)	C1—C2—C3	120.40 (16)
C1 <sup>i</sup> —Sn—Cl1	86.79 (4)	C1—C2—H2	119.8
Cl2—Sn—Cl1	180.0	C3—C2—H2	119.8
C1—Sn—S <sup>i</sup>	86.66 (4)	C4—C3—C2	119.72 (16)
C1 <sup>i</sup> —Sn—S <sup>i</sup>	92.73 (4)	C4—C3—H3	120.1
Cl2—Sn—S <sup>i</sup>	95.405 (10)	C2—C3—H3	120.1
Cl1—Sn—S <sup>i</sup>	84.595 (10)	C5—C4—C3	120.09 (17)
C1—Sn—S	92.73 (4)	C5—C4—H4	120.0
C1 <sup>i</sup> —Sn—S	86.66 (4)	C3—C4—H4	120.0
Cl2—Sn—S	95.405 (10)	C4—C5—C6	120.17 (16)

C11—Sn—S	84.595 (10)	C4—C5—H5	119.9
S <sup>i</sup> —Sn—S	169.19 (2)	C6—C5—H5	119.9
C7—S—Sn	110.52 (6)	C1—C6—C5	120.28 (16)
C7—N1—H1A	119.0 (18)	C1—C6—H6	119.9
C7—N1—H1B	120.9 (17)	C5—C6—H6	119.9
H1A—N1—H1B	120 (2)	N2—C7—N1	119.24 (18)
C7—N2—H2A	120.3 (19)	N2—C7—S	118.15 (15)
C7—N2—H2B	119 (2)	N1—C7—S	122.58 (15)
H2A—N2—H2B	120 (3)		

Symmetry code: (i)  $-x, -y+1/2, z$ .

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1B $\cdots$ Cl2	0.86 (3)	2.50 (3)	3.345 (2)	166 (2)
N2—H2A $\cdots$ Cl1 <sup>ii</sup>	0.81 (3)	2.41 (3)	3.2119 (19)	170 (3)

Symmetry code: (ii)  $-y+3/4, x+1/4, z+1/4$ .