

Substitutional disorder in a hypervalent diorganotin(IV) dihalide

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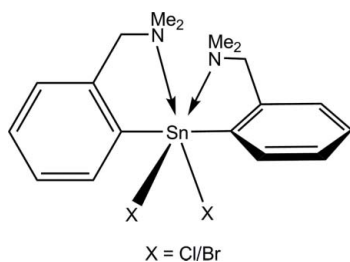
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Key indicators: single-crystal X-ray study; $T = 297$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; disorder in main residue; R factor = 0.026; wR factor = 0.060; data-to-parameter ratio = 16.2.

The structure of bromidochloridobis[2-(dimethylaminomethyl)phenyl]tin(IV), $[\text{SnBr}_{0.65}\text{Cl}_{1.35}(\text{C}_9\text{H}_{12}\text{N})_2]$, contains two 2-(Me_2NCH_2) C_6H_4 units bonded to a Sn atom which lies on a twofold axis. The compound exhibits substitutional disorder of the halide atoms bonded to the Sn, with 1.35 occupancy for Cl and 0.65 for Br; it is isomorphous with the corresponding dichloride. The Sn atom is hexacoordinated with a $(\text{C}_2\text{N})_2\text{SnX}_2$ ($X = \text{Cl}/\text{Br}$) distorted octahedral core as a result of the strong intramolecular $\text{N} \rightarrow \text{Sn}$ coordination *trans* to the $\text{Sn}-\text{X}$ bonds ($\text{N1}-\text{Sn1}-\text{X1} = 165.8^\circ$). As a result of the intermolecular contacts, *viz.* $\text{H} \cdots \text{X}$ and $\text{H} \cdots \text{benzene}$ interactions, the molecules are arranged in a three-dimensional supramolecular manner in the crystal structure.

Related literature

For related literature see Varga *et al.* (2001, 2005, 2006, 2007); Rotar *et al.* (2007); Emsley (1994); IUPAC (1979).



Experimental

Crystal data

$[\text{SnBr}_{0.65}\text{Cl}_{1.35}(\text{C}_9\text{H}_{12}\text{N})_2]$
 $M_r = 486.89$

Monoclinic, $C2/c$
 $a = 17.0221$ (15) Å

$b = 8.2387$ (7) Å
 $c = 14.7510$ (13) Å
 $\beta = 106.1050$ (10)°
 $V = 1987.5$ (3) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 2.78$ mm⁻¹
 $T = 297$ (2) K
 $0.32 \times 0.25 \times 0.11$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SAINT-Plus*; Bruker, 2000)
 $T_{\min} = 0.452$, $T_{\max} = 0.738$

6916 measured reflections
1746 independent reflections
1693 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.060$
 $S = 1.24$
1746 reflections

108 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.47$ e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
C3—H3...Cg1 ⁱⁱ	0.93	3.19	3.78 (1)	123
C4—H4...Cl1 ⁱⁱ /Br1 ⁱⁱⁱ	0.93	2.87	3.798 (5)	173
C6—H6...Cl1 ⁱⁱⁱ /Br1 ⁱⁱⁱ	0.93	3.02	3.710 (3)	132

Symmetry code: (ii) $-\frac{1}{2} + x, \frac{1}{2} + y, z$, (iii) $2 - x, 1 - y, 1 - z$. Cg1 is the centroid of the benzene ring C1–C6.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GD2029).

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supplementary materials

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A. Rotar, R. A. Varga and C. Silvestru

Comment

During our work on hypervalent organotin(IV) compounds with the [2-(Me₂NCH₂)C₆H₄]₂Sn fragment (Varga *et al.*, 2001, 2005, 2006, 2007, Rotar *et al.* 2007), the title compound (I) was isolated. It contains two 2-(Me₂NCH₂)C₆H₄ units bonded to a tin atom which lies on a twofold axis of the space group *C2/c*. The compound exhibits substitutional disorder of both halide atoms bonded to the Sn with chlorine being the major (1.35) and the bromine the minor (0.65) component.

The structure of [2-(Me₂NCH₂)C₆H₄]₂SnCl₂ was also determined (Varga *et al.*, 2001) and is isomorphous with the title compound. Both have space group *C2/c*; the cell constants as well as the volume differ slightly (0.39% increase for the title compound) as the result of the presence of a different halide in the molecular unit.

The molecules of the compound feature a metal atom strongly coordinated by two nitrogen atoms of the pendant arms [Sn—N1 = 2.64 (1) Å; the Sn—N distance exceeds the sum of the covalent radii for the corresponding atoms, $\Sigma_{\text{cov}}(\text{Sn}, \text{N}) = 2.1$ Å (Emsley, 1994)] *trans* to an Sn—halogen bond (N1—Sn1—X1 = 165.8°). This results in a (C,N)₂SnX₂ (X = Cl/Br) core in the title compound with a *trans*-SnC₂ fragment, while the N and X atoms are *cis* positions (Fig. 1). The octahedral geometry around the Sn atom is distorted from the ideal geometry as a consequence of the small 'bite' of the pendant arm ligand [C1—Sn1—N1 = 71.4°] and the steric repulsion between the organic groups bonded to the Sn atoms. All these features are similar to the corresponding dichloride.

As a result of the intramolecular coordination of the nitrogen to the tin atom a five-membered SnC₃N ring is formed. This ring is not planar but is folded along the Sn(1)⋯C_{methylene} axis with the N atom out of the best plane defined by the residual SnC₃, thus inducing planar chirality, with the phenyl ring as chiral plane and the nitrogen as pilot atom (IUPAC, 1979). Indeed, the compound crystallizes as a racemate, *i.e.* a mixture of $R_{\text{N1}}R_{\text{N1}}^i$ and $S_{\text{N1}}S_{\text{N1}}^i$ [symmetry code: (i) 2 - x, y, 0.5 - z].

In the crystal of the title compound intermolecular interactions, *i.e.* hydrogen bond type interactions and H⋯phenyl interactions (Fig. 2), give rise to a supramolecular array. If only chlorine is considered than layers are built of the same type of isomer [H4⋯X1ⁱⁱ = 2.87 Å, H3⋯Cg1ⁱⁱ = 3.19 Å; symmetry code: (ii) -1/2 + x, 1/2 + y, z] along the *ab* plane (Fig. 3). If bromine is taken into account, than alternating parallel layers of $R_{\text{N1}}R_{\text{N1}}^i$ and $S_{\text{N1}}S_{\text{N1}}^i$ isomers are bridged through weak H6⋯X1ⁱⁱⁱ [3.02 Å; symmetry code: (iii) 2 - x, 1 - y, 1 - z] interactions resulting in a three-dimensional supramolecular architecture (Fig. 4).

Experimental

The title compound was isolated as a by-product of the reaction between [2-(Me₂NCH₂)C₆H₄]₂SnCl₂ and [2,6-(Me)₂C₆H₃]₂MgBr, due to partial halide exchange.

Refinement

All hydrogen atoms were placed in calculated positions using a riding model, with C—H = 0.93–0.97 Å and with $U_{\text{iso}} = 1.5U_{\text{eq}}$ (C) for methyl H and $U_{\text{iso}} = 1.2U_{\text{eq}}$ (C) for aryl H. The methyl groups were allowed to rotate but not to tip. The two halide atoms were refined as substitutional disorder between chlorine and bromine, with 1.35 occupancy for Cl and 0.65 occupancy for Br.

Figures

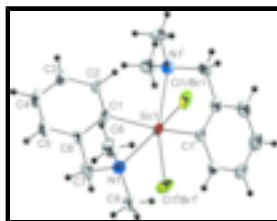


Fig. 1. : A view of title compound showing the atom-numbering scheme at 30% probability thermal ellipsoids for (R_N, R_N^1)-(I) isomer [symmetry code: (i) $2 - x, y, 0.5 - z$]. H atoms are drawn as spheres of arbitrary radii.

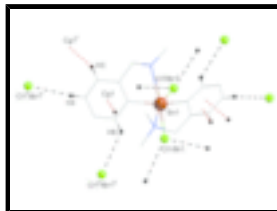


Fig. 2. : Intermolecular interactions [shown as dashed lines, black for $H \cdots X$ ($X = \text{Cl/Br}$), red for $H \cdots \text{phenyl}$]. Only H involved in interactions are shown. Symmetry codes: (i) $2 - x, y, 0.5 - z$, (ii) $-1/2 + x, 1/2 + y, z$, (iii) $2 - x, 1 - y, 1 - z$.

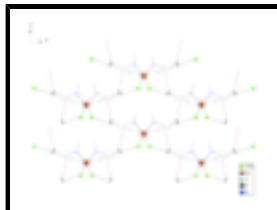


Fig. 3. : View of the two-dimensional layer formed through $H \cdots X$ and $H \cdots \text{phenyl}$ interactions along c axis. Only H involved in interactions are shown.

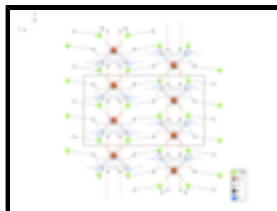


Fig. 4. : Crystal packing showing the three-dimensional supramolecular architecture along a axis. Only H involved in interactions are shown.

bromidochloridobis[2-(dimethylaminomethyl)phenyl]tin(IV)

Crystal data

[SnBr_{0.65}Cl_{1.35}(C₉H₁₂N)₂]

$M_r = 486.89$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 17.0221$ (15) Å

$F_{000} = 966.8$

$D_x = 1.627$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 3754 reflections

$\theta = 2.5\text{--}26.9^\circ$

$b = 8.2387 (7) \text{ \AA}$
 $c = 14.7510 (13) \text{ \AA}$
 $\beta = 106.1050 (10)^\circ$
 $V = 1987.5 (3) \text{ \AA}^3$
 $Z = 4$

$\mu = 2.78 \text{ mm}^{-1}$
 $T = 297 (2) \text{ K}$
 Block, colourless
 $0.32 \times 0.25 \times 0.11 \text{ mm}$

Data collection

Bruker Smart APEX CCD area-detector diffractometer	1746 independent reflections
Radiation source: fine-focus sealed tube	1693 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.035$
$T = 297(2) \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
phi and ω scans	$\theta_{\text{min}} = 2.5^\circ$
Absorption correction: multi-scan (SAINT-Plus; Bruker, 2000)	$h = -19 \rightarrow 20$
$T_{\text{min}} = 0.452, T_{\text{max}} = 0.738$	$k = -9 \rightarrow 9$
6916 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H-atom parameters constrained
$wR(F^2) = 0.060$	$w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 3.2594P]$
$S = 1.24$	where $P = (F_o^2 + 2F_c^2)/3$
1746 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
108 parameters	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$
	Extinction correction: none

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
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supplementary materials

Br1	1.04832 (5)	0.42622 (9)	0.36987 (5)	0.0721 (3)	0.325 (3)
Cl1	1.04832 (5)	0.42622 (9)	0.36987 (5)	0.0721 (3)	0.675 (3)
Sn1	1.0000	0.64336 (4)	0.2500	0.03453 (12)	
C1	0.89182 (18)	0.7072 (4)	0.2862 (2)	0.0386 (7)	
C6	0.8831 (2)	0.6785 (4)	0.3757 (2)	0.0455 (8)	
H6	0.9254	0.6293	0.4212	0.055*	
C2	0.8274 (2)	0.7761 (5)	0.2181 (3)	0.0517 (9)	
C5	0.8125 (2)	0.7221 (5)	0.3982 (3)	0.0589 (10)	
H5	0.8072	0.7022	0.4583	0.071*	
C4	0.7506 (3)	0.7942 (6)	0.3318 (3)	0.0714 (12)	
H4	0.7035	0.8260	0.3472	0.086*	
C3	0.7572 (2)	0.8206 (6)	0.2424 (3)	0.0707 (12)	
H3	0.7141	0.8688	0.1975	0.085*	
N1	0.91474 (19)	0.8322 (4)	0.1136 (2)	0.0547 (8)	
C7	0.8321 (2)	0.7923 (6)	0.1177 (3)	0.0653 (11)	
H7A	0.8150	0.6911	0.0845	0.078*	
H7B	0.7947	0.8766	0.0860	0.078*	
C8	0.9324 (3)	1.0031 (5)	0.1373 (3)	0.0785 (13)	
H8A	0.8954	1.0700	0.0915	0.118*	
H8B	0.9876	1.0269	0.1371	0.118*	
H8C	0.9259	1.0246	0.1987	0.118*	
C9	0.9204 (3)	0.8054 (7)	0.0157 (3)	0.0838 (15)	
H9A	0.8810	0.8724	-0.0273	0.126*	
H9B	0.9096	0.6934	-0.0012	0.126*	
H9C	0.9744	0.8331	0.0124	0.126*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0787 (5)	0.0714 (5)	0.0805 (6)	0.0373 (4)	0.0458 (4)	0.0378 (4)
Cl1	0.0787 (5)	0.0714 (5)	0.0805 (6)	0.0373 (4)	0.0458 (4)	0.0378 (4)
Sn1	0.03419 (18)	0.03473 (18)	0.04017 (19)	0.000	0.01949 (13)	0.000
C1	0.0344 (16)	0.0371 (17)	0.0486 (19)	0.0027 (13)	0.0187 (15)	-0.0014 (14)
C6	0.0446 (19)	0.048 (2)	0.050 (2)	0.0021 (15)	0.0240 (16)	-0.0028 (16)
C2	0.0413 (19)	0.061 (2)	0.056 (2)	0.0070 (17)	0.0187 (17)	0.0090 (18)
C5	0.058 (2)	0.068 (3)	0.063 (2)	0.003 (2)	0.036 (2)	-0.002 (2)
C4	0.052 (2)	0.084 (3)	0.093 (3)	0.015 (2)	0.045 (2)	0.002 (3)
C3	0.044 (2)	0.082 (3)	0.089 (3)	0.018 (2)	0.023 (2)	0.013 (2)
N1	0.0518 (18)	0.068 (2)	0.0470 (17)	0.0091 (15)	0.0181 (14)	0.0161 (15)
C7	0.045 (2)	0.088 (3)	0.059 (2)	0.009 (2)	0.0076 (18)	0.019 (2)
C8	0.090 (3)	0.062 (3)	0.085 (3)	0.004 (2)	0.026 (3)	0.022 (2)
C9	0.084 (3)	0.121 (4)	0.050 (2)	0.019 (3)	0.024 (2)	0.030 (3)

Geometric parameters (\AA , $^\circ$)

Br1—Sn1	2.4893 (7)	C4—H4	0.9300
Sn1—C1	2.121 (3)	C3—H3	0.9300
Sn1—C1 ⁱ	2.121 (3)	N1—C7	1.462 (5)

Sn1—Cl1 ⁱ	2.4893 (7)	N1—C8	1.462 (5)
Sn1—Br1 ⁱ	2.4893 (7)	N1—C9	1.491 (5)
C1—C2	1.387 (5)	C7—H7A	0.9700
C1—C6	1.389 (5)	C7—H7B	0.9700
C6—C5	1.380 (5)	C8—H8A	0.9600
C6—H6	0.9300	C8—H8B	0.9600
C2—C3	1.389 (5)	C8—H8C	0.9600
C2—C7	1.510 (5)	C9—H9A	0.9600
C5—C4	1.360 (6)	C9—H9B	0.9600
C5—H5	0.9300	C9—H9C	0.9600
C4—C3	1.372 (6)		
C1—Sn1—C1 ⁱ	151.30 (17)	C4—C3—C2	120.8 (4)
C1—Sn1—Cl1 ⁱ	102.61 (9)	C4—C3—H3	119.6
C1 ⁱ —Sn1—Cl1 ⁱ	97.93 (9)	C2—C3—H3	119.6
C1—Sn1—Br1 ⁱ	102.61 (9)	C7—N1—C8	110.1 (3)
C1 ⁱ —Sn1—Br1 ⁱ	97.93 (9)	C7—N1—C9	109.2 (3)
Cl1 ⁱ —Sn1—Br1 ⁱ	0.00 (4)	C8—N1—C9	108.0 (3)
C1—Sn1—Br1	97.93 (9)	N1—C7—C2	112.0 (3)
C1 ⁱ —Sn1—Br1	102.61 (9)	N1—C7—H7A	109.2
Cl1 ⁱ —Sn1—Br1	88.11 (4)	C2—C7—H7A	109.2
Br1 ⁱ —Sn1—Br1	88.11 (4)	N1—C7—H7B	109.2
C2—C1—C6	119.2 (3)	C2—C7—H7B	109.2
C2—C1—Sn1	119.1 (2)	H7A—C7—H7B	107.9
C6—C1—Sn1	121.8 (2)	N1—C8—H8A	109.5
C5—C6—C1	120.9 (3)	N1—C8—H8B	109.5
C5—C6—H6	119.6	H8A—C8—H8B	109.5
C1—C6—H6	119.6	N1—C8—H8C	109.5
C1—C2—C3	119.0 (4)	H8A—C8—H8C	109.5
C1—C2—C7	120.0 (3)	H8B—C8—H8C	109.5
C3—C2—C7	120.9 (3)	N1—C9—H9A	109.5
C4—C5—C6	119.6 (4)	N1—C9—H9B	109.5
C4—C5—H5	120.2	H9A—C9—H9B	109.5
C6—C5—H5	120.2	N1—C9—H9C	109.5
C5—C4—C3	120.5 (4)	H9A—C9—H9C	109.5
C5—C4—H4	119.7	H9B—C9—H9C	109.5
C3—C4—H4	119.7		
C1 ⁱ —Sn1—C1—C2	70.1 (3)	C6—C1—C2—C7	-173.7 (4)
Cl1 ⁱ —Sn1—C1—C2	-64.6 (3)	Sn1—C1—C2—C7	4.9 (5)
Br1 ⁱ —Sn1—C1—C2	-64.6 (3)	C1—C6—C5—C4	-0.1 (6)
Br1—Sn1—C1—C2	-154.4 (3)	C6—C5—C4—C3	1.5 (7)
C1 ⁱ —Sn1—C1—C6	-111.4 (3)	C5—C4—C3—C2	-0.8 (7)
Cl1 ⁱ —Sn1—C1—C6	113.9 (3)	C1—C2—C3—C4	-1.3 (7)
Br1 ⁱ —Sn1—C1—C6	113.9 (3)	C7—C2—C3—C4	175.0 (4)
Br1—Sn1—C1—C6	24.1 (3)	C8—N1—C7—C2	-75.8 (4)
C2—C1—C6—C5	-2.0 (5)	C9—N1—C7—C2	165.8 (4)

supplementary materials

Sn1—C1—C6—C5	179.5 (3)	C1—C2—C7—N1	-37.0 (5)
C6—C1—C2—C3	2.6 (6)	C3—C2—C7—N1	146.8 (4)
Sn1—C1—C2—C3	-178.8 (3)		

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

Y—H \cdots π -ring interactions.

<i>Y—H\cdotsCg</i>	<i>Y—H</i>	<i>H\cdotsCg</i>	<i>Y\cdotsCg</i>	<i>Y—H\cdotsCg</i>
C3—H3 \cdots Cg1 ⁱⁱ	0.93	3.19	3.78 (1)	123

Symmetry code: (ii) $-1/2 + x, 1/2 + y, z$. Cg1 is the centroid of the benzene ring C1–C6.

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D—H\cdotsA</i>	<i>D—H</i>	<i>H\cdotsA</i>	<i>D\cdotsA</i>	<i>D—H\cdotsA</i>
C4—H4 \cdots Cl1 ⁱⁱ /Br1 ⁱⁱ	0.93	2.87	3.798 (5)	173
C6—H6 \cdots Cl1 ⁱⁱⁱ /Br1 ⁱⁱⁱ	0.93	3.02	3.710 (3)	132

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

Fig. 1

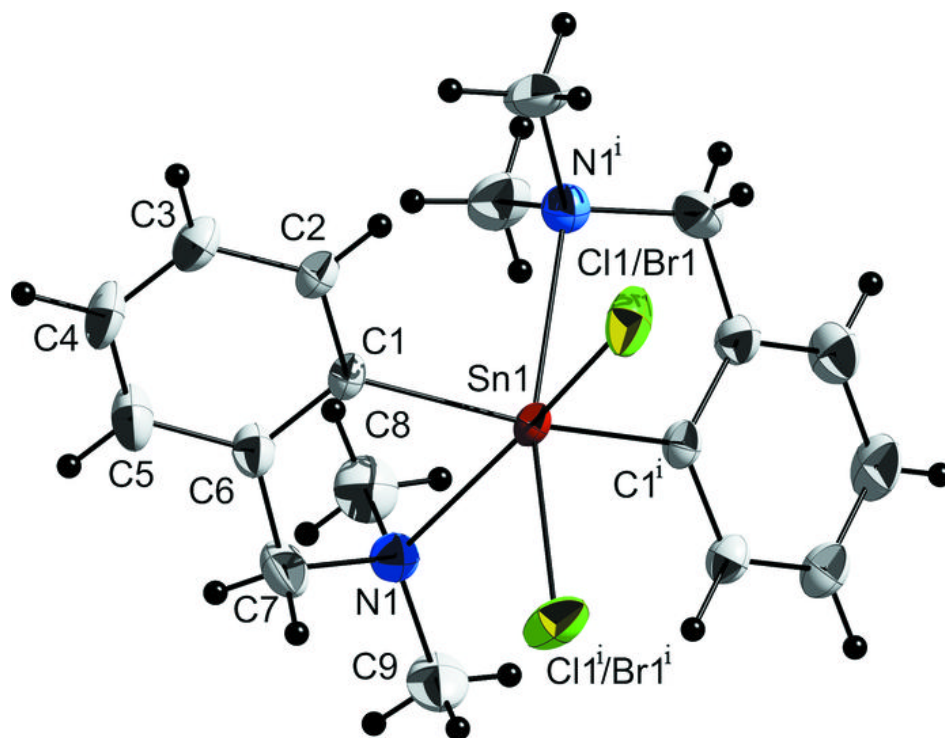


Fig. 2

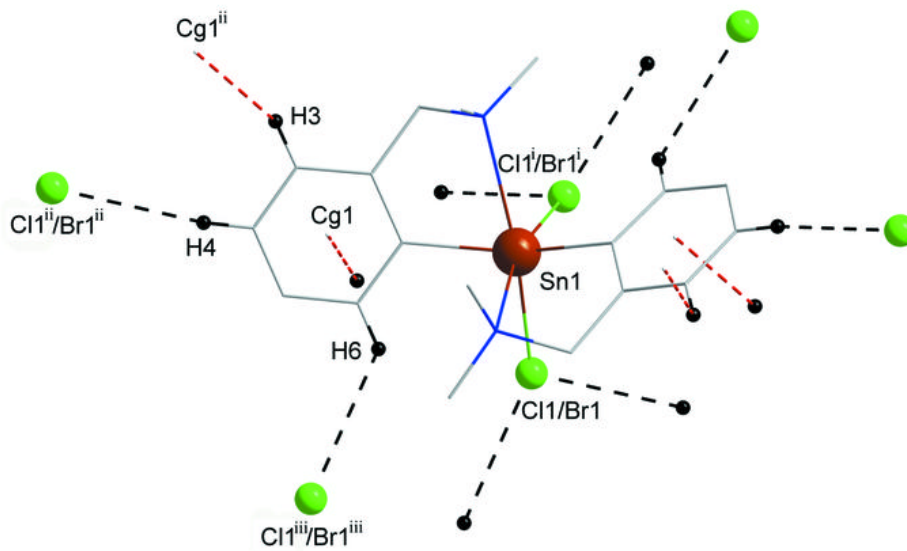


Fig. 3

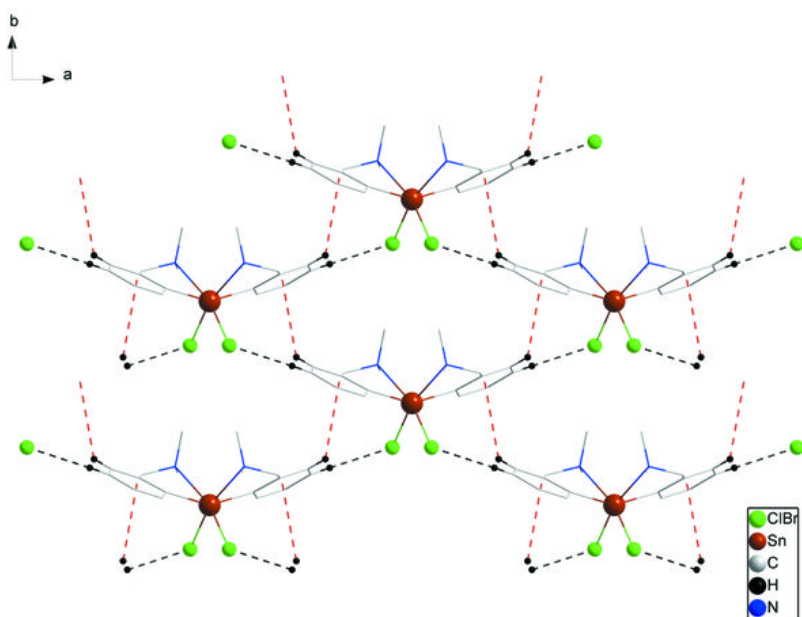


Fig. 4

