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Substitutional disorder in a hypervalent diorganotin(IV) dihalide

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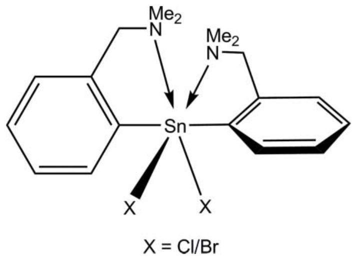
Key indicators: single-crystal X-ray study; T = 297 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.026; wR factor = 0.060; data-to-parameter ratio = 16.2.

The structure of bromidochloridobis[2-(dimethylaminomethyl)phenyl]tin(IV), $[SnBr_{0.65}Cl_{1.35}(C_9H_{12}N)_2]$, 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 $(C,N)_2SnX_2$ (X = Cl/Br) distorted octahedral core as a result of the strong intramolecular N→Sn coordination *trans* to the Sn—X bonds (N1—Sn1—X1 = 165.8°). As a result of the intermolecular contacts, *viz*. H$\cdots X$ and H$\cdots$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

$[SnBr_{0.65}Cl_{1.35}(C_9H_{12}N)_2]$
M_r = 486.89
Monoclinic, $C2/c$
a = 17.0221 (15) Å
b = 8.2387 (7) Å
c = 14.7510 (13) Å
β = 106.1050 (10)°
V = 1987.5 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.78 mm^{-1}
T = 297 (2) K
0.32 × 0.25 × 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_{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
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

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

D—H$\cdots$A	D—H	H$\cdots$A	D$\cdots$A	D—H$\cdots$A
C3—H3$\cdots Cg1^{ii}$	0.93	3.19	3.78 (1)	123
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) $-\frac{1}{2}+x, \frac{1}{2}+y, z$, (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: *publCIF* (Westrip, 2007).

Financial support from the National University Research Council (CEEX 63/2006) is greatly appreciated. We also thank the National Center for X-Ray Diffraction, Cluj-Napoca, for help with the solid-state structure determination.

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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Substitutional disorder in a hypervalent diorganotin(IV) dihalide

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

Comment

During our work on hypervalent organotin(IV) compounds with the [2-(Me_2NCH_2)C_6H_4]Sn fragment (Varga *et al.*, 2001, 2005, 2006, 2007, Rotar *et al.* 2007), the title compound (I) was isolated. It contains two 2-(Me_2NCH_2)C_6H_4 units bonded to a tin atom which lies on a twofold axis of the space group *C*2/*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-(Me_2NCH_2)C_6H_4]$_2$$SnCl_2$ 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, $\Sigma_{cov}(Sn,N)$ = 2.1 Å (Emsley, 1994)] *trans* to an Sn–halogen bond (N1—Sn1—X1 = 165.8°). This results in a $(C,N)_2SnX_2$ (X = Cl/Br) core in the title compound with a *trans*-SnC_2 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 SnC_3N 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 SnC_3, 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 $R_{N1}R_{N1}^{i}$ and $S_{N1}S_{N1}^{i}$ [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···X1^{ii} = 2.87 Å, H3···*Cg*1^{ii} = 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 $R_{N1}R_{N1}^{i}$ and $S_{N1}S_{N1}^{i}$ isomers are bridged through weak H6···X1^{iii} [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-(Me_2NCH_2)C_6H_4]$SnCl_2$ and [2,6-(Me)$_2$$C_6H_3$]MgBr, 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 $U_{\rm iso}$= 1.5$U_{\rm eq}$ (C) for methyl H and $U_{\rm iso}$= 1.2$U_{\rm eq}$ (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

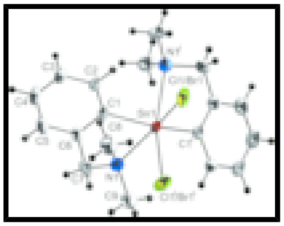

Fig. 1. : A view of title compound showing the atom-numbering scheme at 30% probability thermal ellipsoids for ($R_{\rm N}$,$R_{\rm N}^{\rm i}$)-(I) isomer [symmetry code: (i) 2 − *x*, *y*, 0.5 − *z*]. H atoms are drawn as spheres of arbitrary radii.

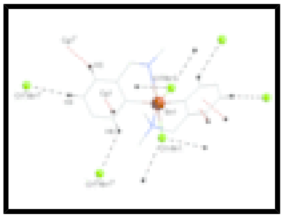

Fig. 2. : Intermolecular interactions [shown as dashed lines, black for H···*X* (*X* = Cl/Br), red for *H*···phenyl]. Only H involved in interactions are showed. Symmetry codes: (i) 2 − *x*, *y*, 0.5 − *z*, (ii) −1/2 + *x*, 1/2 + *y*, *z*, (iii) 2 − *x*, 1 − *y*, 1 − *z*.

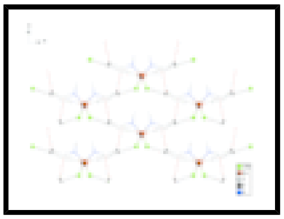

Fig. 3. : View of the two-dimensional layer formed through H···*X* and *H*···phenyl interactions along *c* axis. Only H involved in interactions are showed.

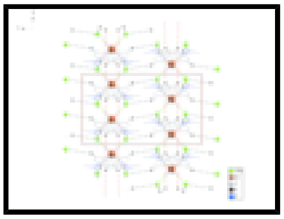

Fig. 4. : Crystal packing showing the three-dimensional supramolecular architecture along *a* axis. Only H involved in interactions are showed.

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

Crystal data

[SnBr$_{0.65}$Cl$_{1.35}$(C$_9$H$_{12}$N)$_2$]

M_r = 486.89

Monoclinic, *C*2/*c*

Hall symbol: -C 2yc

a = 17.0221 (15) Å

F_{000} = 966.8

D_x = 1.627 Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 3754 reflections

θ = 2.5–26.9°

b = 8.2387 (7) Å
c = 14.7510 (13) Å
β = 106.1050 (10)°
V = 1987.5 (3) Å^3
Z = 4

μ = 2.78 mm^{-1}
T = 297 (2) K
Block, colourless
0.32 × 0.25 × 0.11 mm

Data collection

Bruker Smart APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
T = 297(2) K
phi and ω scans
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_{int} = 0.035
$\theta_{\max}$ = 25.0°
$\theta_{\min}$ = 2.5°
$h = -19 \rightarrow 20$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.060
S = 1.24
1746 reflections
108 parameters
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 3.2594P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.36 e Å^{-3}
$\Delta\rho_{\min}$ = −0.46 e Å^{-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 > 2sigma(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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)

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 (Å^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 (Å, °)

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)

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···π-ring interactions.

Y—H···*Cg*	*Y*—H	H···*Cg*	*Y*···*Cg*	*Y*—H···*Cg*
C3—H3···*Cg*1^{ii}	0.93	3.19	3.78 (1)	123

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

Hydrogen-bond geometry (Å, °)

D-H···A	D-H	H···A	D···A	D-H···A
C4-H4···Cl1^{ii}/Br1^{ii}	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) −1/2 + *x*, 1/2 + *y*, *z*, (iii) 2 − *x*, 1 − *y*, 1 − *z*.

Fig. 1

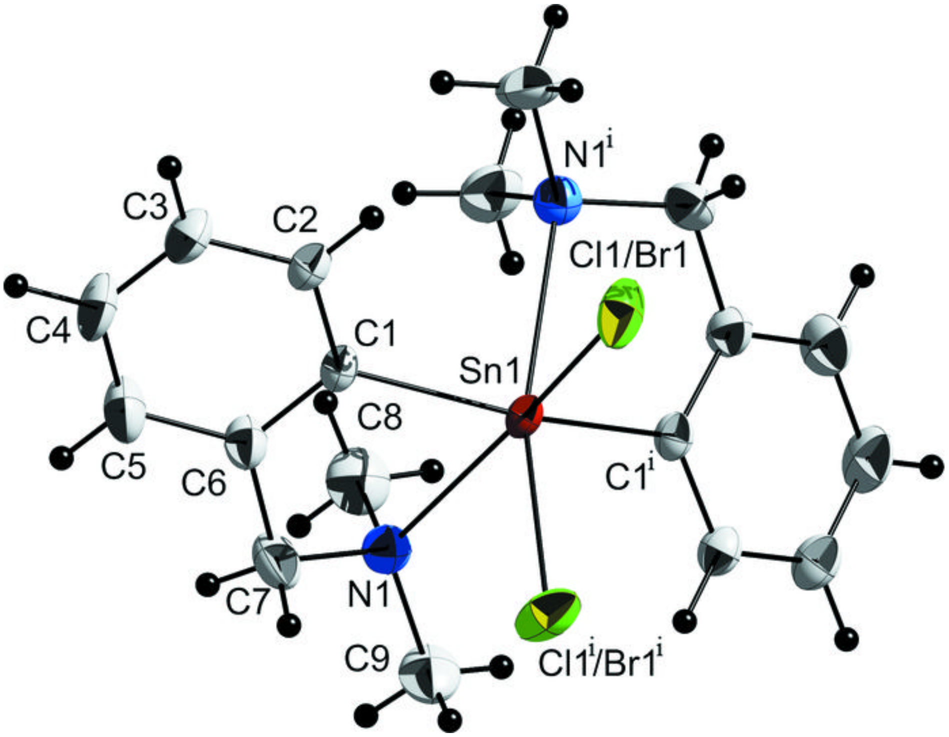

Fig. 2

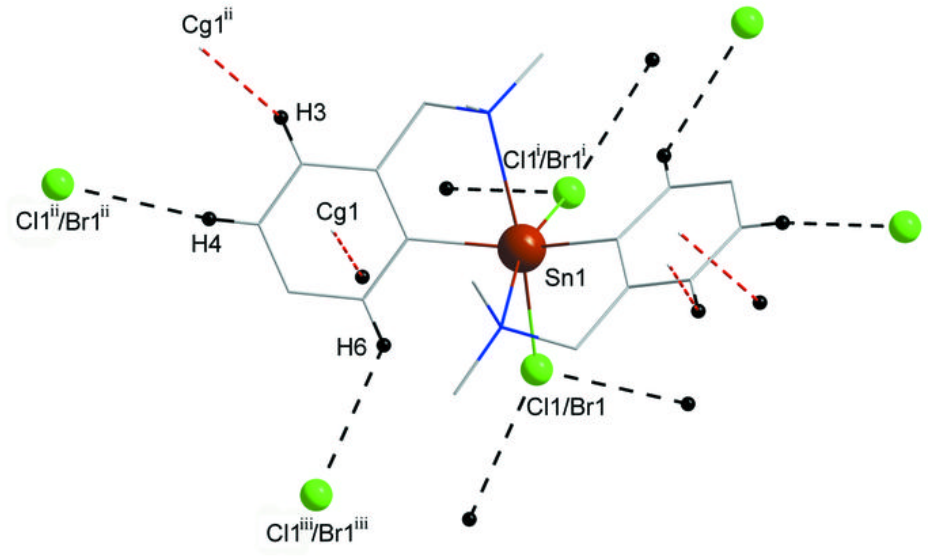
Cg1^{ii}
H3
Cl1^{i}/Br1^{i}
Cl1^{ii}/Br1^{ii}
Cg1
H4
Sn1
H6
Cl1/Br1
Cl1^{iii}/Br1^{iii}

Fig. 3

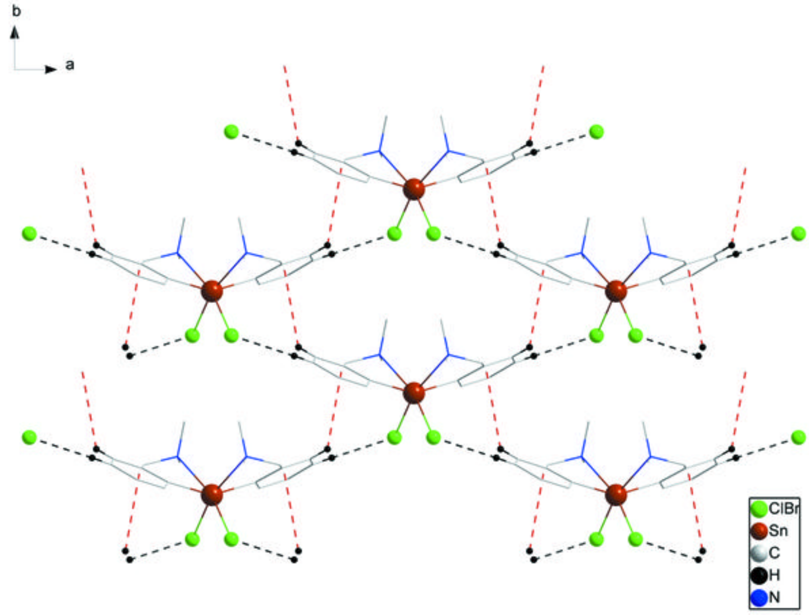

Fig. 4