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Crystal structures of isotypic poly[bis(benzimidazolium) [tetra-μ-iodido-stannate(II)]] and poly[bis(5,6-difluorobenzimidazolium) [tetra-μ-iodido-stannate(II)]]

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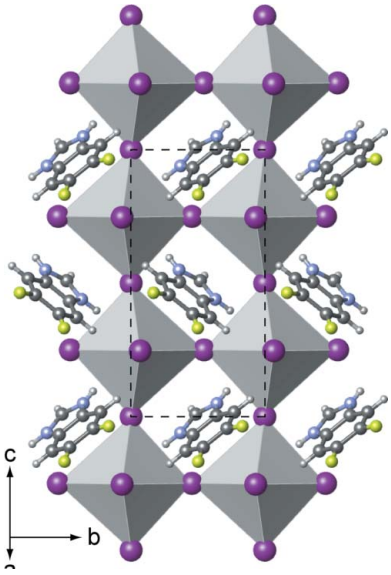
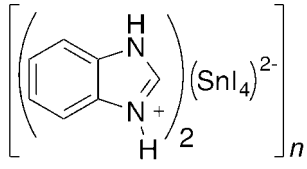
The isostructural title compounds, $\{(C_7H_7N_2)_2[SnI_4]\}_n$, (1), and $\{(C_7H_5F_2N_2)_2[SnI_4]\}_n$, (2), show a layered perovskite-type structure composed of anionic $\{[SnI_4]^{2-}\}_n$ sheets parallel to (100), which are decorated on both sides with templating benzimidazolium or 5,6-difluorobenzimidazolium cations, respectively. These planar organic heterocycles mainly form N—H···I hydrogen bonds to the terminal I atoms of the corner-sharing [SnI_6] octahedra (point group symmetry 2) from the inorganic layer, but not to the bridging ones. This is in contrast to most of the reported structures of related compounds where ammonium cations are involved. Here hydrogen bonding to both types of iodine atoms and thereby a distortion of the inorganic layers to various extents is observed. For (1) and (2), all Sn—I—Sn angles are linear and no out-of-plane distortions of the inorganic layers occur, a fact of relevance in view of the material properties. The arrangement of the aromatic cations is mainly determined through the direction of the N—H···I hydrogen bonds. The coherence between organic bilayers along [100] is mainly achieved through van der Waals interactions.

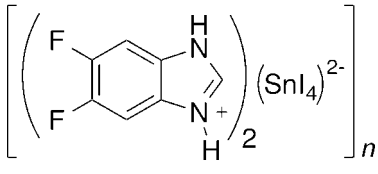
1. Chemical context

The title compounds, (1) and (2), belong to an extensive family of materials exhibiting a perovskite-type structure, which can vary with respect to the dimensionality of its extended inorganic framework, ranging from two-dimensional, $[MX_4]_n^{2n-}$, to three-dimensional, $[MX_3]_n^{n-}$ (Mitzi, 1999, 2001, 2004; Mitzi *et al.*, 2001; Zhengtao *et al.*, 2003*a*,*b*). The former case is exemplified by anionic $[MX_4]_n^{2n-}$ sheets (M = divalent metal ion; X = halogen) of corner-sharing MX_6 octahedra, which are separated by bilayers of organic cations.





(1)



(2)

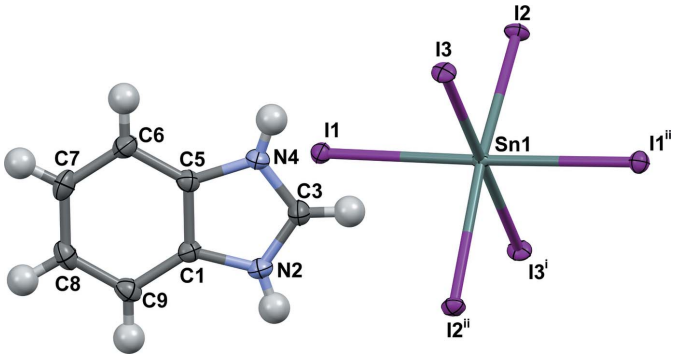


Figure 1
The main building units of (1), showing atom labeling and displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $x, y+1, z$; (ii) $-x, y, -z+\frac{1}{2}$.]

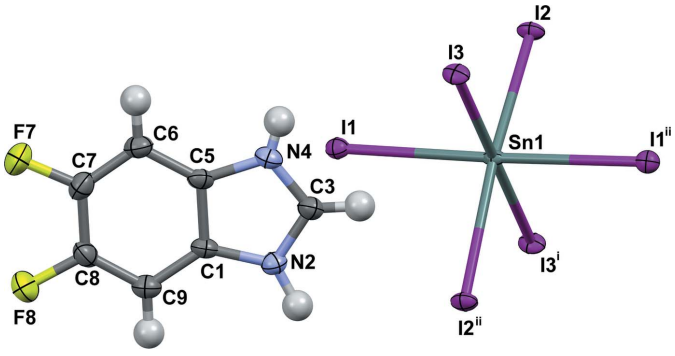


Figure 2
The main building units of (2), showing atom labeling and displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $x, y+1, z$; (ii) $-x, y, -z+\frac{1}{2}$.]

For most reported layered perovskites, these organic molecules are terminated with one or two protonated primary amine groups. Thereby, the ammonium head(s) form N—H$\cdots X$ hydrogen bonds to any of the bridging and terminal halogen atoms in the inorganic layers (Mitzi *et al.*, 2002; Mercier *et al.*, 2004; Sourisseau *et al.*, 2007; Pradeesh *et al.*, 2013). In the actual case, however, as a novel aspect, the bicyclic aromatic benzimidazole unit is introduced as an organic part. There are numerous general examples of benzimidazole acting as a neutral ligand (Keene *et al.*, 2010) and similarly in its protonated form (Mouchaham *et al.*, 2010). In this context, the present study explicitly demonstrates that benzimidazolium cations and corresponding derivatives can stabilize the layered perovskite structure as well, while fitting perfectly into the 'footprint' provided by the inorganic framework. This observation bears importance since the extent of the in- and out-of-plane angular distortions, twisting and buckling of the anionic sheets, is largely determined by the relative charge density, steric requirements and hydrogen-bonding pattern of the organic cations (Knutson & Martin, 2005; Takahashi *et al.*, 2007). These distortions correlate with the band gaps of the perovskite-type semiconductors. It is interesting to note that perovskite-based solar cells have recently been catapulted to the cutting edge of thin-film photovoltaic research (Hao *et al.*, 2014; Marchioro *et al.*, 2014). Consequently, the chemical variability which comes with the imidazolium cation, especially the range of possible substitutions on its molecular skeleton, gives an additional structural diversity to this class of compounds. As a case in point, consider the difluoro-substituted compound (2) which renders not only modified van der Waals interactions for the organic bilayers, but also tailors the 'chemistry' of the crystal surfaces.

Table 1
Selected geometric parameters (Å, °) for (1).

Sn1—I1	3.1571 (2)	Sn1—I3	3.1607 (3)
Sn1—I2	3.1242 (1)	Sn1—I3^{i}	3.0626 (3)
I1—Sn1—I2	89.357 (3)	I2—Sn1—I3	83.886 (4)
I1—Sn1—I2^{ii}	90.984 (3)	I1—Sn1—I3^{i}	88.396 (4)
I1—Sn1—I1^{ii}	176.793 (9)	I2—Sn1—I3^{i}	96.114 (4)
I2—Sn1—I2^{ii}	167.773 (7)	I3—Sn1—I3^{i}	180.0
I1—Sn1—I3	91.604 (4)		

Symmetry codes: (i) $x, y+1, z$; (ii) $-x, y, -z+\frac{1}{2}$.

Table 2
Selected geometric parameters (Å, °) for (2).

Sn1—I1	3.1596 (3)	Sn1—I3	3.1310 (5)
Sn1—I2	3.1129 (1)	Sn1—I3^{i}	3.0491 (5)
I1—Sn1—I2	89.374 (6)	I2—Sn1—I3	84.077 (6)
I1—Sn1—I2^{ii}	90.984 (6)	I1—Sn1—I3^{i}	88.269 (7)
I1—Sn1—I1^{ii}	176.539 (14)	I2—Sn1—I3^{i}	95.923 (6)
I2—Sn1—I2^{ii}	168.154 (12)	I3—Sn1—I3^{i}	180.0
I1—Sn1—I3	91.731 (7)		

Symmetry codes: (i) $x, y+1, z$; (ii) $-x, y, -z+\frac{1}{2}$.

2. Structural commentary

Compounds (1) and (2) are isostructural. Their asymmetric units, Figs. 1 and 2, consist of an Sn^{2+} cation situated on a twofold rotation axis (Wyckoff position 4*e*), three iodine atoms [one in a general position, one on an inversion centre (4*a*) and one on a twofold rotation axis (4*e*)] and a benzimidazolium or 5,6-difluorobenzimidazolium cation, respectively. The main building blocks of the structure are corner-sharing [SnI_6] octahedra, which form planar sheets with formula $\{[SnI_4]^{2-}\}_n$ which extend parallel to (100). The negative charge of these layers is compensated by the organic cations, which are on both sides of the layer, attached by strong hydrogen-bonding and Coulombic interactions (Figs. 3 and 4). This structural motif can be regarded as an *A*–*B*–*A* layer system, where *A* represents the aromatic cation and *B* the tin iodide layer. The coherence between organic bilayers along [100] is mainly achieved through van der Waals interactions. The Sn—I bond lengths for (1) range from 3.0626 (3) Å to 3.1607 (3) Å [(2): 3.0491 (5) Å to 3.1596 (3) Å], with no distinct pattern for bridging compared to terminal iodine atoms (Tables 1 and 2). These values are in agreement with those reported previously for related tin iodide perovskite structures, as for example $[(C_4H_9NH_3)_2[SnI_4]]$, where the bond lengths range from 3.133 Å to 3.16 Å (Mitzi, 1996). The I—Sn—I angles of the

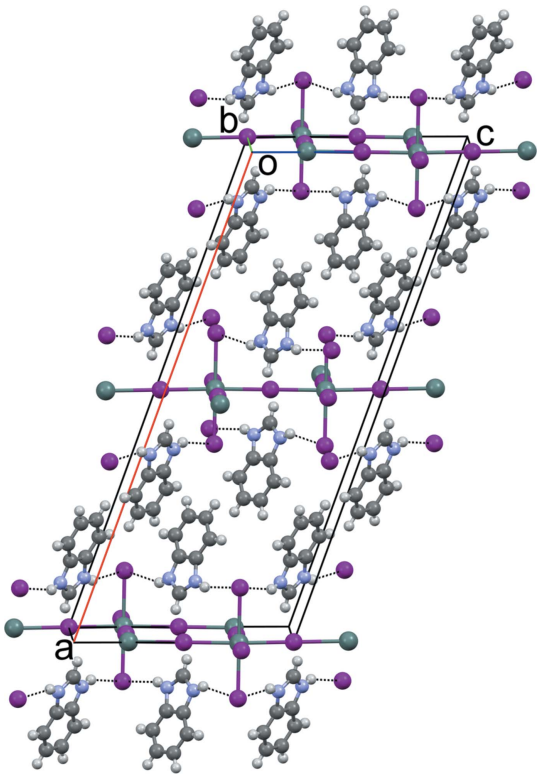


Figure 3
The crystal packing of compound (1) viewed along [010]. N—H···I hydrogen bonds are shown as dashed lines.

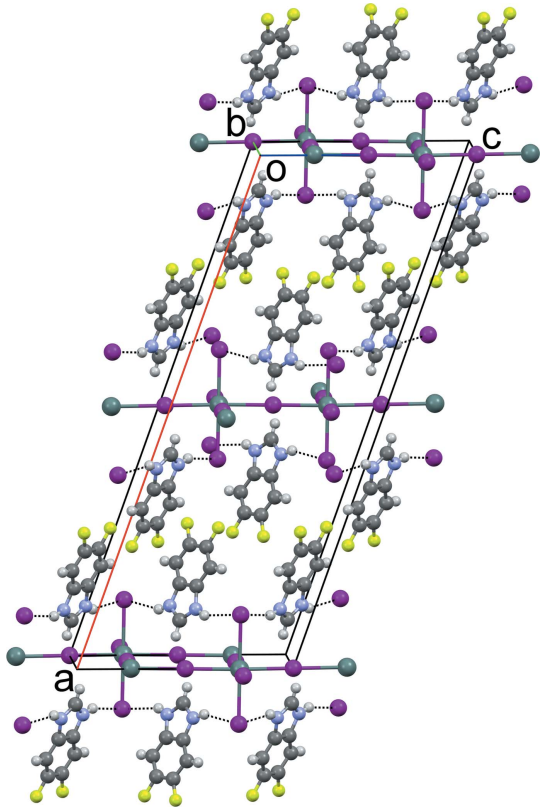


Figure 4
The crystal packing of compound (2) viewed along [010]. N—H···I hydrogen bonds are shown as dashed lines.

Table 3
Hydrogen-bond geometry (Å, °) for (1).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···I1^{iii}	0.81 (3)	2.85 (3)	3.615 (2)	158 (3)
N4—H4···I1^{i}	0.85 (3)	2.86 (3)	3.630 (2)	151 (2)

Symmetry codes: (i) $x, y+1, z$; (iii) $x, -y, z-\frac{1}{2}$.

Table 4
Hydrogen-bond geometry (Å, °) for (2).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···I1^{iii}	0.95 (6)	2.79 (6)	3.610 (4)	145 (4)
N4—H4···I1^{i}	0.75 (5)	2.88 (6)	3.587 (4)	157 (6)

Symmetry codes: (i) $x, y+1, z$; (iii) $x, -y, z-\frac{1}{2}$.

[SnI_6] octahedra in the title structures deviate slightly from the ideal octahedral geometry. With 83.886 (4)° for (1) [(2): 84.077 (6)°], the I2—Sn1—I3 angle has the largest difference. On the other hand, all Sn—I—Sn angles are linear, which leads to the formation of an almost rectangular grid (Fig. 5). There is no out-of-plane distortion of the inorganic sheet. The arrangement of the aromatic cations is mainly determined through the direction of N—H···I hydrogen bonds to the apical iodine atoms (Tables 3 and 4; Figs. 3 and 4). There is no N—H···$I_{bridging}$ contact smaller than the sum of the respective van der Waals radii (H: 1.2, I: 1.98 Å; Bondi, 1964). This is in contrast to primary ammonium cations, which form hydrogen bonds to both apical and bridging iodine atoms. The shortest H···$I_{bridging}$ distance is C3—H3···I2 with 3.12 Å for (1) [(2): 3.19 Å] close to the sum of van der Waals radii. Adjacent cations within an organic layer show a plane-to-plane distance

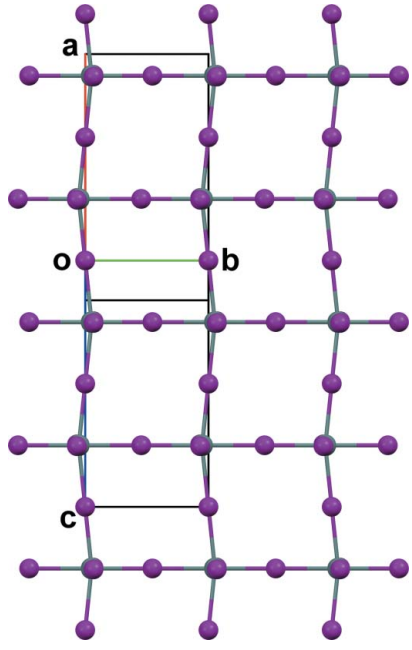


Figure 5
View along the a^* axis of a tin iodide layer of (2). For clarity, the atoms are represented as spheres with uniform sizes selected for each atom type.

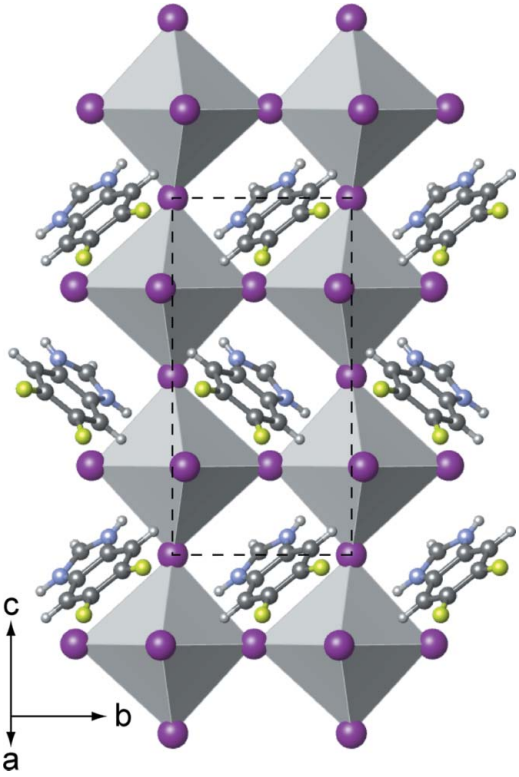


Figure 6
View along the *a** axis of a double layer of tin iodide and the organic cations of (2). For clarity, the [SnI_6] octahedra are shown as polyhedra, the atoms of the organic cations are represented as spheres with uniform sizes selected for each atom type.

of 3.786 Å for (1) [(2): 3.730 Å] (Fig. 6). The shortest contact distances between the organic bilayers for both compounds are close to the sums of the van der Waals radii [C8···H6^{i} 2.801 Å in (1) and F8···H9^{ii} 2.557 Å in (2); (i): $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii): $\frac{1}{2}-x, \frac{1}{2}-y, -z$]. The larger size of the fluorine atom in comparison to the hydrogen atom is reflected in a larger *A*–*B*–*A* layer spacing of 14.407 Å for (2) compared to 13.950 Å for (1).

3. Database survey

In the Cambridge Structural Database (Version 5.35, last update November 2013; Allen, 2002) no structures of compounds containing a (benz)imidazolium cation for layered perovskites are listed, making the two examples presented herein the only ones reported so far.

4. Synthesis and crystallization

Compound (1) was synthesized and crystallized by a solvothermal method using a mixture of tin(II) iodide and benzimidazole in a 1:2 molar ratio. In a 50 ml round-bottom flask, 4 ml concentrated HI (57 wt. %, stabilized with hypophosphorous acid) was mixed with 2 mmol (0.236 g) benzimidazole. After stirring for one minute, this solution was added to a sample flask containing 1 mmol (0.372 g) tin(II) iodide. The reaction flask was put in a 23 ml Teflon container. The reaction was conducted at 363 K for ten h after which the

Table 5
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	$(C_7H_7N_2)_2[SnI_4]$	$(C_7H_5F_2N_2)_2[SnI_4]$
M_r	864.58	936.55
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*
Temperature (K)	123	123
a, *b*, *c* (Å)	29.6316 (5), 6.22328 (10), 12.4258 (2)	31.3825 (6), 6.18011 (12), 12.38507 (13)
β (°)	109.6798 (8)	109.3241 (7)
V (Å^3)	2157.55 (6)	2266.72 (7)
Z	4	4
Radiation type	Mo *K*α	Mo *K*α
μ (mm^{-1})	6.91	6.61
Crystal size (mm)	0.15 × 0.10 × 0.05	0.33 × 0.33 × 0.01
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2001)	Multi-scan (*TWINABS*; Bruker, 2001)
T_{min}, T_{max}	0.570, 0.747	0.322, 0.522
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24695, 3713, 3222	29697, 5792, 5179
R_{int}	0.033	?
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.772	0.768
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.022, 0.045, 1.06	0.035, 0.124, 1.07
No. of reflections	3713	5792
No. of parameters	113	132
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.70, −1.15	1.95, −1.74

Computer programs: *APEX2* and *SAINT-Plus* (Bruker, 2001), *SIR97* (Altomare *et al.*, 1999), *SHELXL2014* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), *VESTA* (Momma & Izumi, 2011) and *publCIF* (Westrip, 2010).

autoclave was slowly cooled (1 K/h) to room temperature. Thin, black plate-like crystals were obtained. The synthetic procedure for (2) was identical to that for (1), only using 0.5 mmol (0.77 g) 5,6-difluorobenzimidazole and 0.25 mmol (0.093 g) tin(II) iodide as starting materials. Thin, black plate-like crystals were obtained.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. The N-H hydrogen atoms were located in difference Fourier maps and were freely refined. The C-bound hydrogen atoms were included in calculated positions and treated as riding atoms with C—H = 0.95 Å. The isotropic displacement parameters of all H atoms were constrained to $1.2U_{eq}$ of their parent atoms. The crystal of compound (2) was a non-merohedral twin. The two twin components were related by a twofold rotation about the c^* axis. The data from both twin components were integrated to give 8236 and 7625 non-overlapped reflections for twin components 1 and 2, respectively, plus 13836 overlapping reflections from both twin components. Symmetry-equivalent reflections were merged. The major twin fraction, component 1, refined to 0.6870 (12).

Acknowledgements

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supporting information

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Crystal structures of isotypic poly[bis(benzimidazolium) [tetra-μ-iodido-stannate(II)]] and poly[bis(5,6-difluorobenzimidazolium) [tetra-μ-iodido-stannate(II)]]

Iwan Zimmermann, Tony D. Keene, Jürg Hauser, Silvio Decurtins and Shi-Xia Liu

Computing details

For both compounds, data collection: *APEX2* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus* (Bruker, 2001); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008) and *VESTA* (Momma & Izumi, 2011); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(1) Poly[bis(benzimidazolium) [tetra-μ-iodido-stannate(II)]]

Crystal data

$(C_7H_7N_2)_2[SnI_4]$
M_r = 864.58
Monoclinic, $C2/c$
a = 29.6316 (5) Å
b = 6.22328 (10) Å
c = 12.4258 (2) Å
β = 109.6798 (8)°
V = 2157.55 (6) Å^3
Z = 4
$F(000)$ = 1552
D_x = 2.662 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9894 reflections
θ = 2.9–33.1°
μ = 6.91 mm^{-1}
T = 123 K
Plate, black
0.15 × 0.10 × 0.05 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.570, T_{max} = 0.747
24695 measured reflections
3713 independent reflections
3222 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 33.3°, θ_{min} = 2.9°
h = −44→45
k = −8→9
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.045
S = 1.06
3713 reflections
113 parameters
0 restraints
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0195P)^2 + 1.2708P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −1.15 e Å^{-3}

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Sn1	0.0000	0.05346 (3)	0.2500	0.01164 (5)
I1	0.11310 (2)	0.06766 (2)	0.33720 (2)	0.01725 (5)
I2	0.0000	0.0000	0.0000	0.01759 (5)
I3	0.0000	−0.45442 (3)	0.2500	0.01775 (5)
C1	0.15716 (9)	0.4629 (4)	0.0612 (2)	0.0185 (5)
N2	0.11246 (8)	0.3669 (4)	0.02976 (18)	0.0233 (4)
H2	0.1040 (10)	0.271 (5)	−0.017 (2)	0.028*
C3	0.08537 (9)	0.4715 (4)	0.0783 (2)	0.0244 (5)
H3	0.0530	0.4374	0.0692	0.029*
N4	0.11030 (7)	0.6311 (4)	0.14131 (18)	0.0218 (4)
H4	0.0991 (10)	0.726 (5)	0.175 (2)	0.026*
C5	0.15559 (8)	0.6333 (4)	0.1327 (2)	0.0192 (5)
C6	0.19471 (9)	0.7684 (4)	0.1792 (2)	0.0259 (5)
H6	0.1937	0.8850	0.2278	0.031*
C7	0.23491 (9)	0.7241 (5)	0.1511 (2)	0.0290 (6)
H7	0.2626	0.8114	0.1821	0.035*
C8	0.23624 (10)	0.5553 (4)	0.0788 (2)	0.0270 (6)
H8	0.2646	0.5321	0.0610	0.032*
C9	0.19775 (9)	0.4211 (4)	0.0323 (2)	0.0247 (5)
H9	0.1988	0.3059	−0.0169	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.01576 (10)	0.00942 (10)	0.01029 (10)	0.000	0.00511 (8)	0.000
I1	0.01570 (8)	0.01759 (8)	0.01778 (8)	−0.00079 (5)	0.00476 (6)	−0.00078 (5)
I2	0.02292 (11)	0.01962 (11)	0.01103 (10)	−0.00274 (9)	0.00676 (8)	−0.00021 (8)
I3	0.02441 (11)	0.00891 (10)	0.02168 (11)	0.000	0.01005 (9)	0.000
C1	0.0188 (11)	0.0171 (12)	0.0178 (11)	0.0025 (9)	0.0035 (9)	0.0000 (9)
N2	0.0235 (11)	0.0231 (11)	0.0228 (11)	−0.0026 (9)	0.0073 (9)	−0.0078 (9)
C3	0.0188 (12)	0.0264 (14)	0.0282 (14)	−0.0015 (10)	0.0084 (10)	−0.0034 (11)
N4	0.0212 (10)	0.0219 (11)	0.0235 (11)	0.0002 (9)	0.0092 (9)	−0.0062 (9)
C5	0.0199 (11)	0.0186 (11)	0.0187 (11)	0.0027 (10)	0.0059 (9)	0.0005 (9)
C6	0.0240 (13)	0.0264 (13)	0.0248 (13)	−0.0027 (11)	0.0049 (10)	−0.0057 (11)
C7	0.0184 (12)	0.0337 (15)	0.0290 (14)	−0.0031 (11)	0.0002 (10)	−0.0004 (12)
C8	0.0201 (12)	0.0331 (15)	0.0298 (14)	0.0061 (11)	0.0111 (11)	0.0055 (11)
C9	0.0246 (13)	0.0262 (13)	0.0244 (13)	0.0067 (11)	0.0096 (11)	0.0006 (10)

Geometric parameters (Å, º)

Sn1—I1	3.1571 (2)	N4—C5	1.382 (3)
Sn1—I2	3.1242 (1)	N4—H4	0.85 (3)
Sn1—I3	3.1607 (3)	C5—C6	1.390 (3)
Sn1—I3^{i}	3.0626 (3)	C6—C7	1.377 (4)
C1—N2	1.384 (3)	C6—H6	0.9500
C1—C9	1.390 (3)	C7—C8	1.392 (4)
C1—C5	1.394 (3)	C7—H7	0.9500
N2—C3	1.326 (3)	C8—C9	1.374 (4)
N2—H2	0.81 (3)	C8—H8	0.9500
C3—N4	1.325 (3)	C9—H9	0.9500
C3—H3	0.9500		
I1—Sn1—I2	89.357 (3)	C1—N2—H2	124 (2)
I1—Sn1—I2^{ii}	90.984 (3)	N4—C3—N2	109.6 (2)
I1—Sn1—I1^{ii}	176.793 (9)	N4—C3—H3	125.2
I2—Sn1—I2^{ii}	167.773 (7)	N2—C3—H3	125.2
I1—Sn1—I3	91.604 (4)	C3—N4—C5	108.9 (2)
I2—Sn1—I3	83.886 (4)	C3—N4—H4	125.2 (19)
I1—Sn1—I3^{i}	88.396 (4)	C5—N4—H4	125.5 (19)
I2—Sn1—I3^{i}	96.114 (4)	N4—C5—C6	132.0 (2)
I3—Sn1—I3^{i}	180.0	N4—C5—C1	106.5 (2)
I3^{i}—Sn1—I2^{ii}	96.113 (4)	C6—C5—C1	121.5 (2)
I3^{i}—Sn1—I1^{ii}	88.396 (4)	C7—C6—C5	116.4 (2)
I2—Sn1—I1^{ii}	90.984 (3)	C7—C6—H6	121.8
I2^{ii}—Sn1—I1^{ii}	89.357 (3)	C5—C6—H6	121.8
I2^{ii}—Sn1—I3	83.887 (4)	C6—C7—C8	122.0 (3)
I1^{ii}—Sn1—I3	91.604 (4)	C6—C7—H7	119.0
Sn1^{iii}—I2—Sn1	180.0	C8—C7—H7	119.0
Sn1^{iv}—I3—Sn1	180.0	C9—C8—C7	122.0 (2)
N2—C1—C9	132.5 (2)	C9—C8—H8	119.0
N2—C1—C5	105.9 (2)	C7—C8—H8	119.0
C9—C1—C5	121.6 (2)	C8—C9—C1	116.5 (2)
C3—N2—C1	109.2 (2)	C8—C9—H9	121.8
C3—N2—H2	127 (2)	C1—C9—H9	121.8
C9—C1—N2—C3	−178.0 (3)	C9—C1—C5—C6	−0.5 (4)
C5—C1—N2—C3	0.2 (3)	N4—C5—C6—C7	−179.3 (3)
C1—N2—C3—N4	−0.7 (3)	C1—C5—C6—C7	−0.2 (4)
N2—C3—N4—C5	0.8 (3)	C5—C6—C7—C8	0.9 (4)
C3—N4—C5—C6	178.5 (3)	C6—C7—C8—C9	−0.9 (4)
C3—N4—C5—C1	−0.7 (3)	C7—C8—C9—C1	0.1 (4)
N2—C1—C5—N4	0.3 (3)	N2—C1—C9—C8	178.6 (3)
C9—C1—C5—N4	178.7 (2)	C5—C1—C9—C8	0.6 (4)
N2—C1—C5—C6	−179.0 (2)		

Symmetry codes: (i) x, y+1, z; (ii) −x, y, −z+1/2; (iii) −x, −y, −z; (iv) x, y−1, z.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···I1^{v}	0.81 (3)	2.85 (3)	3.615 (2)	158 (3)
N4—H4···I1^{i}	0.85 (3)	2.86 (3)	3.630 (2)	151 (2)

Symmetry codes: (i) *x*, *y*+1, *z*; (v) *x*, −*y*, *z*−1/2.

(2) Poly[bis(5,6-difluorobenzimidazolium) [tetra-*μ*-iodido-stannate(II)]]

Crystal data

$(C_7H_5F_2N_2)_2[SnI_4]$
M_r = 936.55
Monoclinic, *C*2/*c*
a = 31.3825 (6) Å
b = 6.18011 (12) Å
c = 12.38507 (13) Å
β = 109.3241 (7)°
V = 2266.72 (7) Å^3
Z = 4
F(000) = 1680
D_x = 2.744 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 9949 reflections
θ = 5.5–65.4°
μ = 6.61 mm^{-1}
T = 123 K
Plate, black
0.33 × 0.33 × 0.01 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
rotation method scans
Absorption correction: multi-scan (*TWINABS*; Bruker, 2001)
T_{min} = 0.322, T_{max} = 0.522
29697 measured reflections
5792 independent reflections
5179 reflections with $I > 2\sigma(I)$
θ_{max} = 33.1°, θ_{min} = 2.8°
h = −47→43
k = 0→9
l = 0→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.124
S = 1.07
5792 reflections
132 parameters
0 restraints
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0948P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.95 e Å^{-3}
$\Delta\rho_{min}$ = −1.74 e Å^{-3}

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. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Sn1	0.0000	0.05198 (5)	0.2500	0.01458 (10)
I1	0.10663 (2)	0.06742 (4)	0.33581 (3)	0.02019 (10)
I2	0.0000	0.0000	0.0000	0.02079 (11)

I3	0.0000	−0.45465 (5)	0.2500	0.02092 (11)
C1	0.14859 (19)	0.4618 (7)	0.0571 (4)	0.0227 (9)
N2	0.10624 (15)	0.3704 (7)	0.0285 (3)	0.0249 (8)
H2	0.092 (2)	0.260 (10)	−0.025 (5)	0.030*
C3	0.08158 (18)	0.4824 (8)	0.0780 (5)	0.0271 (10)
H3	0.0511	0.4521	0.0709	0.033*
N4	0.10586 (15)	0.6417 (7)	0.1383 (3)	0.0251 (8)
H4	0.099 (2)	0.714 (9)	0.178 (5)	0.030*
C5	0.14871 (16)	0.6384 (8)	0.1291 (4)	0.0232 (9)
C6	0.18595 (18)	0.7714 (8)	0.1732 (4)	0.0283 (10)
H6	0.1860	0.8918	0.2210	0.034*
C7	0.22244 (18)	0.7166 (9)	0.1429 (5)	0.0319 (11)
F7	0.26085 (11)	0.8325 (7)	0.1827 (3)	0.0460 (9)
C8	0.22240 (19)	0.5394 (9)	0.0718 (5)	0.0307 (12)
F8	0.26118 (12)	0.5015 (6)	0.0508 (4)	0.0447 (8)
C9	0.18591 (19)	0.4095 (9)	0.0276 (4)	0.0279 (10)
H9	0.1861	0.2901	−0.0205	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.0230 (2)	0.00982 (18)	0.01224 (19)	0.000	0.00759 (19)	0.000
I1	0.02280 (16)	0.01818 (15)	0.01977 (16)	−0.00088 (9)	0.00728 (14)	−0.00114 (10)
I2	0.0304 (2)	0.02089 (19)	0.01304 (19)	−0.00124 (18)	0.00977 (19)	−0.00007 (13)
I3	0.0319 (2)	0.00964 (17)	0.0243 (2)	0.000	0.0134 (2)	0.000
C1	0.029 (3)	0.022 (2)	0.019 (2)	0.0032 (17)	0.0095 (19)	−0.0028 (15)
N2	0.027 (2)	0.022 (2)	0.0249 (19)	−0.0011 (17)	0.0085 (17)	−0.0036 (16)
C3	0.030 (3)	0.029 (2)	0.024 (2)	−0.002 (2)	0.012 (2)	−0.0046 (19)
N4	0.030 (2)	0.023 (2)	0.025 (2)	0.0035 (17)	0.0123 (18)	−0.0023 (16)
C5	0.027 (2)	0.026 (2)	0.0158 (18)	0.0022 (18)	0.0064 (17)	−0.0023 (17)
C6	0.035 (3)	0.026 (2)	0.025 (2)	−0.003 (2)	0.010 (2)	−0.0064 (18)
C7	0.027 (2)	0.034 (3)	0.030 (2)	−0.006 (2)	0.004 (2)	−0.003 (2)
F7	0.0326 (18)	0.055 (2)	0.048 (2)	−0.0165 (17)	0.0106 (16)	−0.0163 (19)
C8	0.024 (3)	0.042 (3)	0.027 (3)	0.005 (2)	0.011 (2)	−0.002 (2)
F8	0.0299 (18)	0.057 (2)	0.050 (2)	0.0018 (16)	0.0168 (19)	−0.0133 (19)
C9	0.034 (3)	0.026 (2)	0.025 (2)	0.001 (2)	0.011 (2)	−0.0035 (18)

Geometric parameters (Å, º)

Sn1—I1	3.1596 (3)	C3—H3	0.9500
Sn1—I2	3.1129 (1)	N4—C5	1.387 (6)
Sn1—I3	3.1310 (5)	N4—H4	0.75 (5)
Sn1—I3^{i}	3.0491 (5)	C5—C6	1.385 (7)
Sn1—I1^{ii}	3.1596 (3)	C6—C7	1.361 (7)
C1—C9	1.376 (7)	C6—H6	0.9500
C1—N2	1.378 (7)	C7—F7	1.348 (6)
C1—C5	1.408 (6)	C7—C8	1.404 (7)
N2—C3	1.330 (7)	C8—F8	1.347 (6)

N2—H2	0.95 (6)	C8—C9	1.357 (8)
C3—N4	1.316 (7)	C9—H9	0.9500
I1—Sn1—I2	89.374 (6)	C1—N2—H2	131 (3)
I1—Sn1—I2^{ii}	90.984 (6)	N4—C3—N2	109.6 (5)
I1—Sn1—I1^{ii}	176.539 (14)	N4—C3—H3	125.2
I2—Sn1—I2^{ii}	168.154 (12)	N2—C3—H3	125.2
I1—Sn1—I3	91.731 (7)	C3—N4—C5	109.7 (4)
I2—Sn1—I3	84.077 (6)	C3—N4—H4	125 (5)
I1—Sn1—I3^{i}	88.269 (7)	C5—N4—H4	124 (5)
I2—Sn1—I3^{i}	95.923 (6)	C6—C5—N4	132.3 (4)
I3—Sn1—I3^{i}	180.0	C6—C5—C1	122.3 (5)
I3^{i}—Sn1—I2^{ii}	95.923 (6)	N4—C5—C1	105.3 (4)
I2^{ii}—Sn1—I3	84.077 (6)	C7—C6—C5	114.9 (4)
I3^{i}—Sn1—I1^{ii}	88.270 (7)	C7—C6—H6	122.6
I2—Sn1—I1^{ii}	90.984 (6)	C5—C6—H6	122.6
I2^{ii}—Sn1—I1^{ii}	89.374 (6)	F7—C7—C6	119.9 (5)
I3—Sn1—I1^{ii}	91.730 (7)	F7—C7—C8	117.4 (5)
Sn1^{iii}—I2—Sn1	180.0	C6—C7—C8	122.7 (5)
Sn1^{iv}—I3—Sn1	180.0	F8—C8—C9	121.0 (5)
C9—C1—N2	131.9 (4)	F8—C8—C7	116.3 (5)
C9—C1—C5	121.7 (5)	C9—C8—C7	122.7 (5)
N2—C1—C5	106.3 (4)	C8—C9—C1	115.6 (5)
C3—N2—C1	109.1 (4)	C8—C9—H9	122.2
C3—N2—H2	119 (3)	C1—C9—H9	122.2
C9—C1—N2—C3	−179.2 (6)	C1—C5—C6—C7	−0.8 (7)
C5—C1—N2—C3	0.5 (6)	C5—C6—C7—F7	−178.7 (5)
C1—N2—C3—N4	−0.5 (6)	C5—C6—C7—C8	0.3 (8)
N2—C3—N4—C5	0.2 (6)	F7—C7—C8—F8	0.4 (8)
C3—N4—C5—C6	178.4 (5)	C6—C7—C8—F8	−178.7 (5)
C3—N4—C5—C1	0.1 (6)	F7—C7—C8—C9	179.2 (5)
C9—C1—C5—C6	0.9 (8)	C6—C7—C8—C9	0.2 (9)
N2—C1—C5—C6	−178.9 (4)	F8—C8—C9—C1	178.7 (5)
C9—C1—C5—N4	179.4 (5)	C7—C8—C9—C1	−0.2 (8)
N2—C1—C5—N4	−0.4 (5)	N2—C1—C9—C8	179.4 (5)
N4—C5—C6—C7	−178.9 (5)	C5—C1—C9—C8	−0.4 (8)

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*, *y*, −*z*+1/2; (iii) −*x*, −*y*, −*z*; (iv) *x*, *y*−1, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···I1^{v}	0.95 (6)	2.79 (6)	3.610 (4)	145 (4)
N4—H4···I1^{i}	0.75 (5)	2.88 (6)	3.587 (4)	157 (6)

Symmetry codes: (i) *x*, *y*+1, *z*; (v) *x*, −*y*, *z*−1/2.