



# Synthesis, X-ray diffraction and Hirshfeld surface analysis of two new hybrid dihydrate compounds: $(C_6H_{22}N_4)[SnCl_6]Cl_2 \cdot 2H_2O$ and $(C_8H_{24}N_4)[SnCl_6]Cl_2 \cdot 2H_2O$

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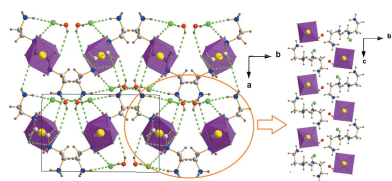
Two new organic–inorganic hybrid compounds, triethylenetetraammonium hexachloridostannate (IV) dichloride dihydrate,  $(C_6H_{22}N_4)[SnCl_6]Cl_2 \cdot 2H_2O$ , (I), and 1,4-bis(2-ammonioethyl)piperazin-1,4-dium hexachloridostannate (IV) dichloride dihydrate,  $(C_8H_{24}N_4)[SnCl_6]Cl_2 \cdot 2H_2O$ , (II), have been synthesized from the same starting materials. In each case both the cations and anions are located about inversion centers. Their crystal structures exhibits alternating inorganic and organic stacking sheets in (I) and layers in (II), with  $Cl^-$  ions and water molecules occupying the space in between. The cohesion of the three-dimensional frameworks are governed by  $N-H \cdots Cl$ ,  $N-H \cdots O$ ,  $C-H \cdots Cl$  and  $O-H \cdots Cl$  hydrogen bonds. Hirshfeld surface analysis of both crystal structures indicates that the  $H \cdots Cl/Cl \cdots H$  contacts exert an important influence on the stabilization of the packing.

## 1. Chemical context

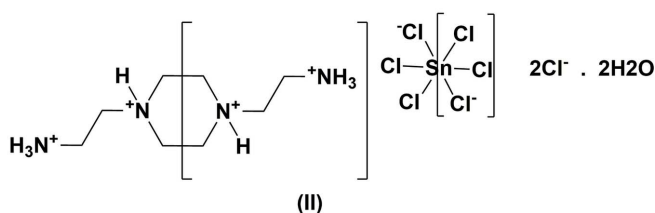
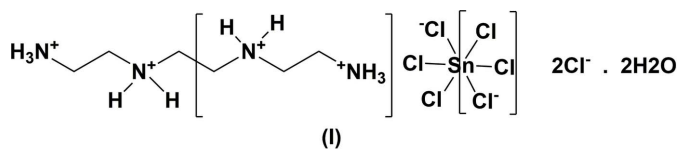
The introduction of organic components into inorganic systems, to form organic–inorganic hybrid materials, has attracted considerable attention since one would expect new properties that are absent in either of their building blocks (Boopathi *et al.*, 2017; Newman *et al.*, 1989; Chun & Jung, 2009). Moreover, halogenostannate hybrid compounds containing protonated amine cations have received considerable attention thanks to their interesting physical and chemical properties, such as magnetic, electroluminescence, photoluminescence and conductivity, which could lead to technological innovations (Aruta *et al.*, 2005; Chouaib *et al.*, 2015; Papavassiliou *et al.*, 1999; Yin & Yo, 1998). Their structures are generally characterized by isolated or connected chains or clusters of  $MX_6$  octahedra separated by the cations.

In this category of materials, the organic moieties, balancing the negative charge on the inorganic parts, usually act as structure-directing agents and greatly affect the structure and the dimensionality of the supramolecular framework (Díaz *et al.*, 2006; Hannon *et al.*, 2002). Furthermore, the experimental conditions employed, such as the solvent, temperature and crystallization method, can also have an important impact on the structure of the final assembly.

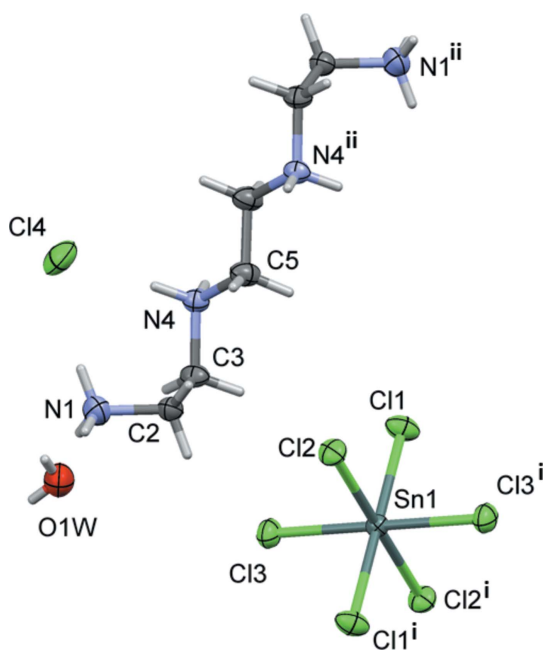
As an extension of our previous studies on hybrid N-containing organic halogenometalate materials (Bouacida *et al.*, 2007, 2009; Bouchene *et al.*, 2014), a flexible aliphatic amino template, triethylenetetraamine (TETA), was reacted



with  $\text{SnCl}_2$  in HCl-acidified aqueous solution. By controlling the temperature, two new organic–inorganic hybrid compounds, triethylenetetraammonium hexachloridostannate(IV) dichloride dihydrate,  $(\text{C}_6\text{H}_{22}\text{N}_4)[\text{SnCl}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (I), and 1,4-bis(2-ammonioethyl)piperazin-1,4-ium, hexachloridostannate (IV) dichloride dihydrate,  $(\text{C}_8\text{H}_{24}\text{N}_4)[\text{SnCl}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (II), were obtained.



Commercial triethylenetetramine is a mixture of linear TETA (typically 60%) and other branched or cyclic TETA, with close boiling points, such as tris-(2-aminoethyl)amine), 1,4-bis(2-aminoethyl)piperazine, (Bis AEP), and *N*-[(2-aminoethyl)2-aminoethyl]piperazine). Piperazine derivatives are relatively more volatile than the corresponding linear polyethylene amines (Hutchinson *et al.*, 1945).



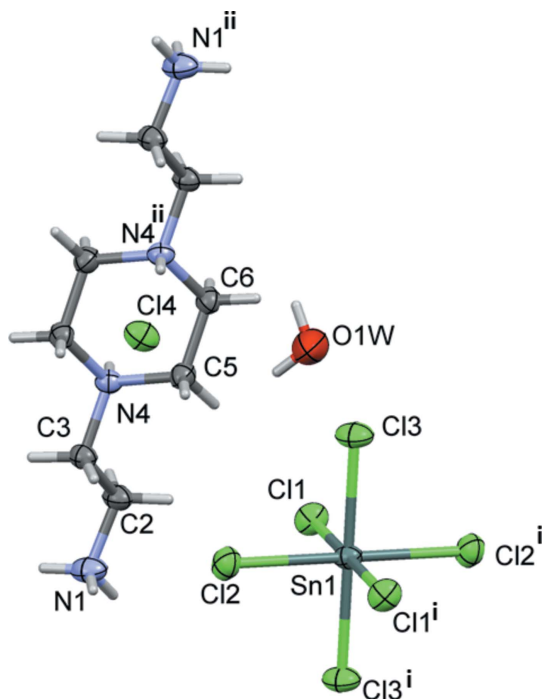
**Figure 1**  
The molecular structure of compound (I), with the atom-numbering scheme for the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level. Only one  $\text{Cl}^-$  anion and one water molecule are shown. [Symmetry codes: (i)  $-x + 1, -y + 2, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 1$ .]

The syntheses of (I) and (II) were carried out with the same starting materials but under different reaction temperatures [343 K for (I) and room temperature for (II)]. Surprisingly, compound (II) was obtained from the reaction of cyclic 1,4-bis(2-aminoethyl)piperazine molecules with  $\text{SnCl}_2$  salt. Under very mild reaction conditions, we believe that (Bis AEP) is present as an impurity in commercial TETA based on the fact that rearrangement reactions of aliphatic chelating polyamines require high pressure and temperature (Liu *et al.*, 2015). Similar undesired reactions have occurred with the same organic cation (Cukrowski *et al.*, 2012; Junk & Smith, 2005; Jiang *et al.*, 2009; Ye *et al.*, 2002).

## 2. Structural commentary

The asymmetric unit of (I) consists of one half of a  $[\text{TETA}]^{4+}$  cation, one half of an inorganic  $[\text{SnCl}_6]^{2-}$  dianion, one  $\text{Cl}^-$  ion and one molecule of water (Fig. 1). The  $[\text{TETA}]^{4+}$  cation is located about a center of symmetry situated at the middle of the central  $-\text{CH}_2-\text{CH}_2-$  bond. The hexachloridostannate(IV) dianion  $[\text{SnCl}_6]^{2-}$ , lying on a centre of inversion, exhibits a nearly perfect octahedral coordination sphere with  $\text{Sn}-\text{Cl}$  bond lengths ranging from 2.4114 (6) to 2.4469 (6) Å and  $\text{Cl}-\text{Sn}-\text{Cl}$  bond angles between 88.94 (2) and 91.06 (2)°.

The asymmetric unit of compound (II) contains one half of a  $[\text{Bis AEP}]^{4+}$  cation, one independent molecule of water, one  $\text{Cl}^-$  ion and half of an  $[\text{SnCl}_6]^{2-}$  dianion lying on a centre of inversion (Fig. 2). The  $[\text{Bis AEP}]^{4+}$  cation is also located about



**Figure 2**  
The molecular structure of compound (II), with the atom-numbering scheme for the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level. Only one  $\text{Cl}^-$  anion and one water molecule are shown. [Symmetry codes: (i)  $-x + 1, -y + 1, -z$ ; (ii)  $-x + 1, -y + 1, -z + 1$ .]

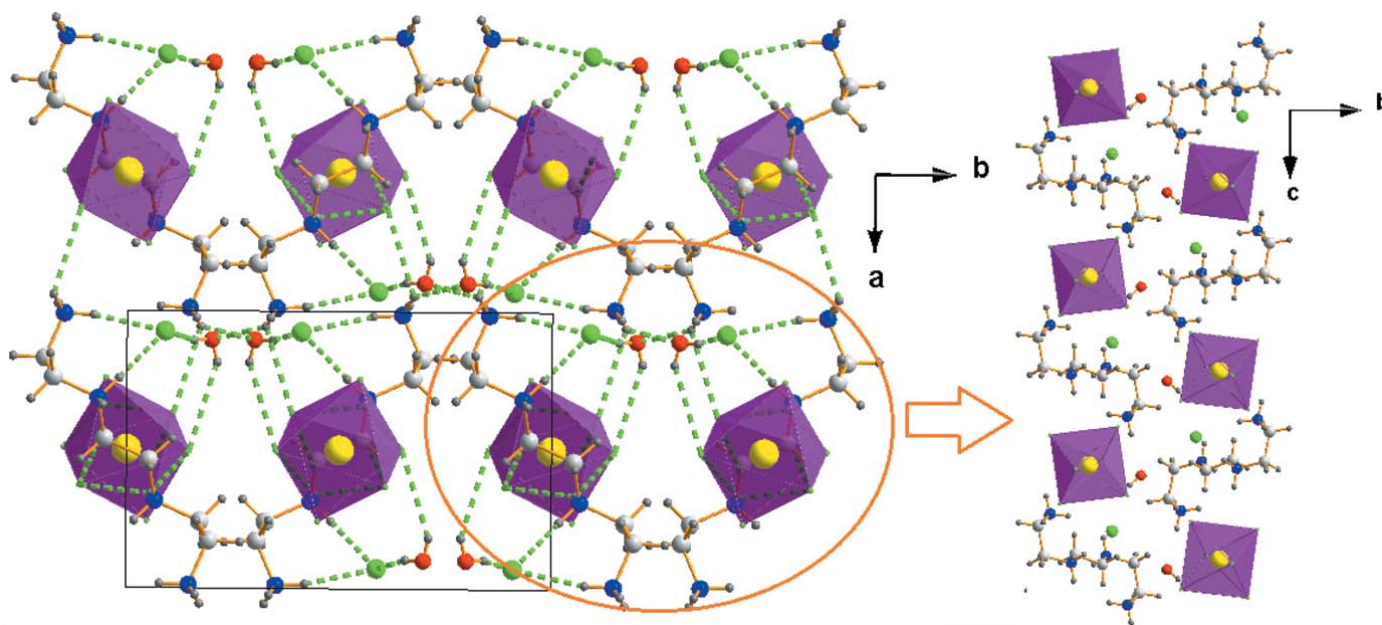


Figure 3  
Projection of the crystal packing of (I) with dashed lines representing hydrogen bonds.

a center of symmetry situated at the center of the piperazin-1,4-dium ring. The nearly perfect octahedral coordination around the  $\text{Sn}^{\text{IV}}$  atom is characterized by  $\text{Sn}-\text{Cl}$  bond lengths varying from 2.4265 (6) to 2.4331 (6) Å and  $\text{Cl}-\text{Sn}-\text{Cl}$  bond angles ranging from 88.55 (2) to 91.45 (2)° for the *cis* angles [180° for *trans* angles]. The organic part is totally protonated and the piperazinium portion adopts a chair conformation, with both ammonioethyl groups being in equatorial positions.

### 3. Supramolecular features

The crystal structure of (I) has an arrangement that can be described as alternating organic  $[\text{TETA}]^{4+}$  and inorganic  $[\text{SnCl}_6]^{2-}$  sheets extending along the *a*-axis direction. The organic cations in adjacent chains are oriented in opposite directions, forming antiparallel sheets. The isolated chloride ions  $\text{Cl}^-$  and the water molecules are located in the otherwise empty space between the sheets (Fig. 3).

The crystal packing of (I) is supported by  $\text{N}-\text{H}\cdots\text{Cl}$ ,  $\text{N}-\text{H}\cdots\text{OW}$  and  $\text{C}-\text{H}\cdots\text{Cl}$  hydrogen-bonding interactions (Table 1). The  $\text{NH}_3^+$  group as well as the  $\text{NH}_2^+$  group of  $[\text{TETA}]^{4+}$  act as hydrogen-bond donors. The  $D\cdots A$  distances for the  $\text{NH}_3^+$  group range from 2.980 (4) to 3.255 (3) Å, while  $D\cdots A$  distances of 3.026 (2) to 3.452 (2) Å are found for the  $\text{NH}_2^+$  group. The water molecules play an important role in stabilizing the crystal packing of (I) because of their strong ability to form hydrogen bonds with both hydrogen-bond donors and acceptors. By acting as hydrogen-bond donors, they bridge isolated  $\text{Cl}^-$  anions and  $[\text{SnCl}_6]^{2-}$  dianions via  $\text{O1W}-\text{H1W}\cdots\text{Cl4}$  and  $\text{O1W}-\text{H2W}\cdots\text{Cl2}$  hydrogen bonds with a  $\text{H}\cdots\text{Cl}$  distances of 2.60 (5) and 2.82 (5) Å, respectively. Additionally, by playing the role of acceptors, the water molecules link the inorganic moieties with the organic cations through  $\text{N1}^+-\text{H1B}\cdots\text{O1W}$  and  $\text{N1}^+-\text{H1C}\cdots\text{O1W}$  charge-assisted hydrogen bonds with  $\text{H}\cdots\text{O}$  distances of 2.09 and 2.25 Å, respectively.

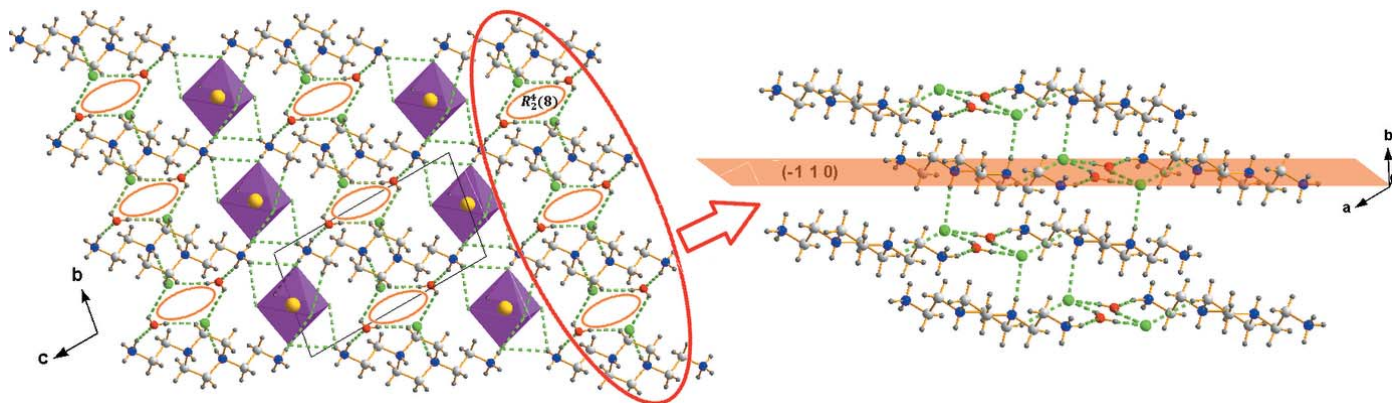


Figure 4  
Detail of the hydrogen-bonding interactions in the crystal structure of (II). Hydrogen bonds are shown as green dashed lines.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ Cl4	0.89	2.30	3.172 (2)	167
N1—H1B $\cdots$ O1W	0.89	2.09	2.980 (4)	179
N1—H1C $\cdots$ Cl1 <sup>i</sup>	0.89	2.75	3.255 (3)	117
N1—H1C $\cdots$ O1W <sup>ii</sup>	0.89	2.25	3.037 (4)	147
O1W—H1W $\cdots$ Cl4 <sup>iii</sup>	0.75 (4)	2.60 (5)	3.281 (3)	151 (4)
O1W—H2W $\cdots$ Cl2 <sup>i</sup>	0.72 (5)	2.82 (5)	3.422 (3)	144 (4)
N4—H4A $\cdots$ Cl2 <sup>ii</sup>	0.90	2.50	3.2225 (19)	138
N4—H4A $\cdots$ Cl1 <sup>iv</sup>	0.90	2.75	3.452 (2)	136
N4—H4B $\cdots$ Cl4	0.90	2.13	3.026 (2)	173
C5—H5B $\cdots$ Cl1 <sup>v</sup>	0.97	2.76	3.445 (3)	128

Symmetry codes: (i)  $x-1, -y+\frac{3}{2}, z-\frac{1}{2}$ ; (ii)  $x, -y+\frac{3}{2}, z+\frac{1}{2}$ ; (iii)  $-x, -y+1, -z$ ; (iv)  $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$ ; (v)  $x, -y+\frac{3}{2}, z-\frac{1}{2}$ .

In (II), the isolated chloride ions, located between the [Bis AEP]<sup>4+</sup> cations, are joined to their adjacent water molecules through strong OW—H $\cdots$ Cl hydrogen bonds, leading to a hydrogen-bonding pattern with a  $R_2^4(8)$  ring motif. The resulting rings, comprising N1<sup>+</sup>—H1B $\cdots$ O1W and C6—H5B $\cdots$ Cl4 hydrogen bonds, promote the formation of sheets of cations aligned parallel to the  $(\bar{1}10)$  plane (Table 2, Fig. 4). These sheets are linked to each other by charge-assisted iminium-N4<sup>+</sup>—H4 $\cdots$ Cl4 hydrogen bonds, leading to the formation of organic layers parallel to the  $ab$  plane. The inorganic layers are built up from isolated [SnCl<sub>6</sub>]<sup>2-</sup> octahedra and alternate with the organic planes along the  $c$ -axis direction. Each anion is hydrogen bonded to adjacent organic cations through atoms N1 and C2 acting as donors of N—H $\cdots$ Cl and C—H $\cdots$ Cl hydrogen bonds with N $\cdots$ Cl distances

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

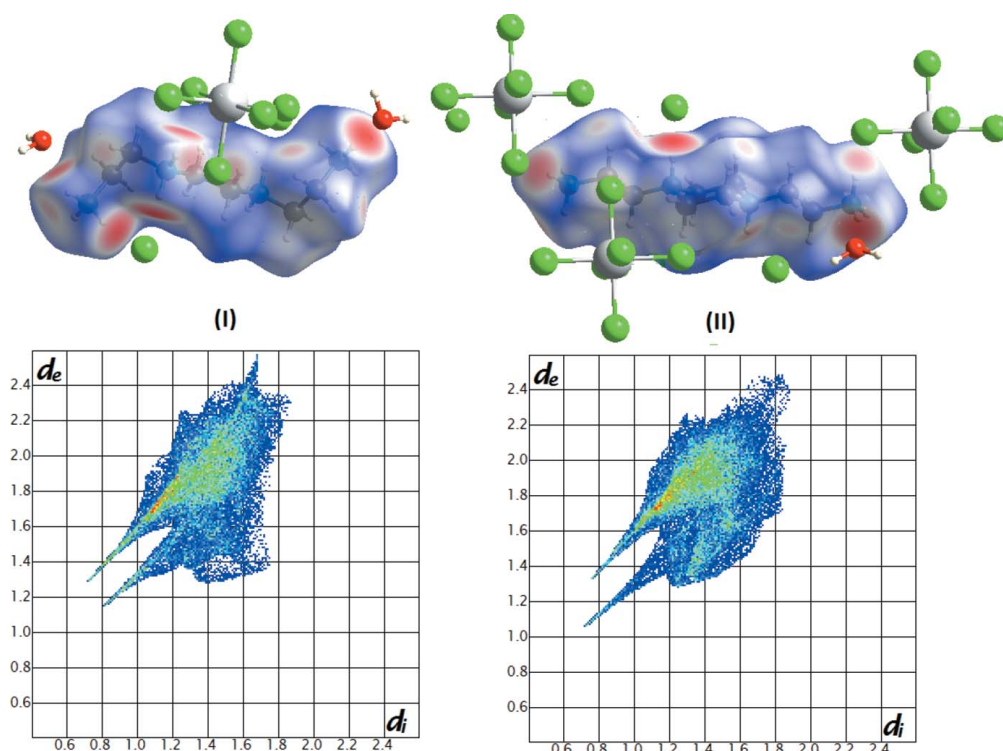
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ Cl3 <sup>i</sup>	0.89	2.71	3.397 (2)	134
N1—H1A $\cdots$ Cl2 <sup>ii</sup>	0.89	2.81	3.431 (2)	128
N1—H1B $\cdots$ Cl1 <sup>iii</sup>	0.89	2.47	3.343 (2)	167
N1—H1C $\cdots$ O1W <sup>i</sup>	0.89	1.92	2.769 (4)	158
O1W—H1W $\cdots$ Cl4 <sup>iv</sup>	0.83 (2)	2.30 (3)	3.079 (3)	158 (6)
O1W—H2W $\cdots$ Cl4	0.83 (4)	2.67 (5)	3.246 (3)	128 (5)
N4—H4 $\cdots$ Cl4	0.85 (4)	2.24 (4)	3.073 (2)	164 (3)
C2—H2B $\cdots$ Cl1	0.97	2.79	3.715 (3)	160
C6—H6A $\cdots$ Cl4 <sup>v</sup>	0.97	2.70	3.506 (3)	141

Symmetry codes: (i)  $x-1, y-1, z$ ; (ii)  $-x, -y, -z$ ; (iii)  $-x, -y+1, -z$ ; (iv)  $-x+1, -y+2, -z+1$ ; (v)  $x+1, y, z$ .

varying from 3.343 (2) to 3.431 (2) Å and the C $\cdots$ Cl distances of 3.715 (3) Å.

#### 4. Hirshfeld surface analysis

The intermolecular interactions of the obtained structures have been quantified using Hirshfeld surface analysis. *CrystalExplorer* software (Wolff *et al.*, 2007) was used to generate the Hirshfeld surface and two-dimensional fingerprint (FP) plots. The analysis of the intermolecular interactions through the mapping of  $d_{\text{norm}}$  is permitted by the contact distances  $d_i$  and  $d_e$  from the Hirshfeld surface to the nearest atom inside and outside, respectively. The surface mapped over  $d_{\text{norm}}$  displays red spots that correspond to contacts shorter than the sum of the van der Waals radii, as shown in Fig. 5.



**Figure 5**  
A view of the Hirshfeld surface mapped over  $d_{\text{norm}}$  and two-dimensional fingerprint plots for compounds (I) and (II).

**Table 3**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	(C <sub>6</sub> H <sub>22</sub> N <sub>4</sub> )[SnCl <sub>6</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O	(C <sub>8</sub> H <sub>24</sub> N <sub>4</sub> )[SnCl <sub>6</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O
<i>M<sub>r</sub></i>	588.62	614.65
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	295	295
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.7573 (2), 12.8372 (3), 9.7103 (2)	7.0856 (2), 7.3269 (2), 12.1624 (4)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 107.265 (1), 90	93.614 (2), 101.357 (1), 117.021 (2)
<i>V</i> (Å <sup>3</sup> )	1042.44 (4)	543.01 (3)
<i>Z</i>	2	1
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	2.26	2.17
Crystal size (mm)	0.12 × 0.04 × 0.03	0.13 × 0.12 × 0.11
Data collection		
Diffractometer	Nonius KappaCCD	Nonius KappaCCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.665, 0.871	0.745, 0.893
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	4666, 2394, 2133	4329, 2494, 2319
<i>R</i> <sub>int</sub>	0.016	0.014
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.650	0.650
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.027, 0.065, 1.17	0.025, 0.064, 1.13
No. of reflections	2394	2494
No. of parameters	104	117
No. of restraints	0	2
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
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.84, -0.75	0.61, -0.65

Computer programs: *COLLECT* (Nonius, 1998), *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *DIAMOND* (Brandenburg & Berndt, 2001).

In compounds (I) and (II), isolated Cl atoms act as potential acceptors for hydrogen bonds; this explains why the greatest contribution to the Hirshfeld surface [65.9% for (I) and 59.8% for (II)] is from the H···Cl/Cl···H contacts. As expected in organic compounds, the H···H contacts are the second important contribution, *i.e.* 24.8% and 30.7% for (I) and (II), respectively. It is evident that van der Waals forces exert an important influence on the stabilization of the packing in the crystal structure. Since both compounds are hydrated, the fingerprint plots also show H···O/O···H contacts that contribute less to the Hirshfeld surfaces, making contributions of 9.3 and 9.5%, respectively.

## 5. Database survey

A search of the Cambridge Structural Database (Version 5.38, update May 2017; Groom *et al.*, 2016) revealed no obvious analogues of (I) and (II) in the crystallographic literature. The structures of related hydrated salts with the same cations, *i.e.* triethylenetetraminium bis(sulfate) monohydrate, (C<sub>6</sub>H<sub>22</sub>N<sub>4</sub>)-SO<sub>4</sub>·H<sub>2</sub>O (III), and bis(2-ammonioethyl)piperazin-1,4-ium tetraperchlorate tetrahydrate, (C<sub>8</sub>H<sub>24</sub>N<sub>4</sub>)<sub>4</sub>ClO<sub>4</sub>·4H<sub>2</sub>O (IV), have been reported (Fu *et al.*, 2005; Ye *et al.*, 2002). Compound (III) was obtained indirectly by a hydrothermal synthesis using a mixture of ferric sulfate nonahydrate and triethylenetetraamine. The ionic product (IV) was also an unexpected product from the reaction between triethylenetetraamine and

perchloric acid. The cationic portion of the structure adopts a chair conformation and the experimental distances are close to those for the neutral ligand.

## 6. Synthesis and crystallization

All chemicals were used without further purification. A solution of an aqueous mixture of tin chloride (SnCl<sub>2</sub>) and tetraethylenetetraamine in an HCl-acidified medium with a stoichiometric ratio of 1:1 was refluxed for one h at 343 K for (I) and room temperature for (II). After two weeks of slow solvent evaporation, single crystals suitable for X-ray analysis were obtained.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Approximate positions for all H atoms were first obtained from difference-Fourier maps. H atoms were then placed idealized positions and refined using the riding-atom approximation: C—H = 0.93 Å and N—H = 0.86 Å, with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C,N). H atoms of the water molecule were located in a difference-Fourier map and refined with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O).

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## supporting information

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## Synthesis, X-ray diffraction and Hirshfeld surface analysis of two new hybrid dihydrate compounds: $(\text{C}_6\text{H}_{22}\text{N}_4)[\text{SnCl}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and $(\text{C}_8\text{H}_{24}\text{N}_4)[\text{SnCl}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

Rafika Bouchene, Zohir Lecheheb, Ratiba Belhouas and Sofiane Bouacida

### Computing details

For both structures, data collection: *COLLECT* (Nonius, 199); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

### Triethylenetetraammonium hexachloridostannate(IV) dichloride dihydrate (I)

#### Crystal data

$(\text{C}_6\text{H}_{22}\text{N}_4)[\text{SnCl}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

$M_r = 588.62$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.7573$  (2) Å

$b = 12.8372$  (3) Å

$c = 9.7103$  (2) Å

$\beta = 107.265$  (1)°

$V = 1042.44$  (4) Å<sup>3</sup>

$Z = 2$

$F(000) = 584$

$D_x = 1.875$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2499 reflections

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

$\mu = 2.26$  mm<sup>-1</sup>

$T = 295$  K

Needle, colorless

$0.12 \times 0.04 \times 0.03$  mm

#### Data collection

Nonius KappaCCD

diffractometer

Radiation source: Enraf Nonius FR590

Graphite monochromator

Detector resolution: 9 pixels mm<sup>-1</sup>

CCD rotation images, thick slices scans

Absorption correction: multi-scan

(SADABS; Krause et al., 2015)

$T_{\min} = 0.665$ ,  $T_{\max} = 0.871$

4666 measured reflections

2394 independent reflections

2133 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 3.2^\circ$

$h = -11 \rightarrow 11$

$k = -16 \rightarrow 16$

$l = -12 \rightarrow 12$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.065$

$S = 1.17$

2394 reflections

104 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

$$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 0.5523P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.003$   
 $\Delta\rho_{\max} = 0.84 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.75 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Sn1	0.5	1	0.5	0.02085 (8)
Cl3	0.24253 (8)	0.95074 (5)	0.52198 (7)	0.03506 (15)
Cl1	0.63022 (8)	0.88957 (5)	0.70418 (7)	0.03609 (16)
Cl2	0.49558 (7)	0.85219 (5)	0.33975 (6)	0.03185 (15)
N4	0.3155 (2)	0.56699 (15)	0.5183 (2)	0.0258 (4)
H4A	0.3399	0.5572	0.6141	0.031*
H4B	0.2434	0.5182	0.4751	0.031*
C5	0.4621 (3)	0.5521 (2)	0.4738 (3)	0.0339 (6)
H5A	0.5376	0.6075	0.5136	0.041*
H5B	0.4352	0.5552	0.3695	0.041*
O1W	-0.1031 (3)	0.69980 (19)	-0.0541 (3)	0.0483 (6)
H1W	-0.107 (5)	0.657 (3)	-0.108 (5)	0.072*
H2W	-0.183 (6)	0.713 (3)	-0.054 (5)	0.072*
Cl4	0.07323 (11)	0.41040 (6)	0.34986 (8)	0.0520 (2)
N1	0.0113 (3)	0.64761 (18)	0.2588 (3)	0.0431 (6)
H1A	0.0167	0.5788	0.2701	0.065*
H1B	-0.0239	0.6629	0.1653	0.065*
H1C	-0.0557	0.6737	0.3032	0.065*
C2	0.1726 (3)	0.69341 (19)	0.3220 (3)	0.0287 (5)
H2A	0.1665	0.7681	0.3058	0.034*
H2B	0.2446	0.6649	0.2726	0.034*
C3	0.2409 (3)	0.67290 (18)	0.4817 (3)	0.0286 (5)
H3A	0.321	0.7254	0.523	0.034*
H3B	0.1561	0.6804	0.5265	0.034*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Sn1	0.02192 (13)	0.02125 (13)	0.01970 (13)	-0.00032 (7)	0.00668 (9)	0.00003 (7)
Cl3	0.0287 (3)	0.0335 (3)	0.0469 (4)	-0.0049 (2)	0.0173 (3)	-0.0010 (3)



C11	0.0401 (4)	0.0393 (3)	0.0293 (3)	0.0120 (3)	0.0110 (3)	0.0106 (3)
C12	0.0358 (3)	0.0287 (3)	0.0298 (3)	0.0001 (2)	0.0079 (3)	-0.0077 (2)
N4	0.0284 (10)	0.0262 (10)	0.0225 (9)	0.0025 (8)	0.0069 (8)	0.0012 (8)
C5	0.0337 (13)	0.0328 (14)	0.0399 (14)	0.0088 (11)	0.0181 (11)	0.0088 (11)
O1W	0.0394 (12)	0.0462 (13)	0.0578 (14)	-0.0046 (10)	0.0122 (11)	-0.0039 (10)
Cl4	0.0690 (5)	0.0346 (4)	0.0455 (4)	-0.0195 (4)	0.0064 (4)	-0.0031 (3)
N1	0.0338 (13)	0.0401 (13)	0.0473 (14)	-0.0031 (10)	-0.0002 (11)	0.0069 (11)
C2	0.0270 (12)	0.0276 (12)	0.0308 (12)	0.0023 (9)	0.0073 (10)	0.0040 (10)
C3	0.0335 (13)	0.0245 (11)	0.0281 (12)	0.0051 (10)	0.0094 (10)	-0.0020 (9)

*Geometric parameters (Å, °)*

Sn1—Cl3	2.4114 (6)	C5—H5B	0.97
Sn1—Cl3 <sup>i</sup>	2.4114 (6)	O1W—H1W	0.75 (4)
Sn1—Cl1	2.4288 (6)	O1W—H2W	0.72 (4)
Sn1—Cl1 <sup>i</sup>	2.4288 (6)	N1—C2	1.484 (3)
Sn1—Cl2	2.4469 (6)	N1—H1A	0.89
Sn1—Cl2 <sup>i</sup>	2.4469 (6)	N1—H1B	0.89
N4—C5	1.484 (3)	N1—H1C	0.89
N4—C3	1.505 (3)	C2—C3	1.510 (3)
N4—H4A	0.9	C2—H2A	0.97
N4—H4B	0.9	C2—H2B	0.97
C5—C5 <sup>ii</sup>	1.512 (5)	C3—H3A	0.97
C5—H5A	0.97	C3—H3B	0.97
Cl3—Sn1—Cl3 <sup>i</sup>	180	C5 <sup>ii</sup> —C5—H5A	109.6
Cl3—Sn1—Cl1	89.97 (2)	N4—C5—H5B	109.6
Cl3 <sup>i</sup> —Sn1—Cl1	90.03 (2)	C5 <sup>ii</sup> —C5—H5B	109.6
Cl3—Sn1—Cl1 <sup>i</sup>	90.03 (2)	H5A—C5—H5B	108.1
Cl3 <sup>i</sup> —Sn1—Cl1 <sup>i</sup>	89.97 (2)	H1W—O1W—H2W	109 (5)
Cl1—Sn1—Cl1 <sup>i</sup>	180	C2—N1—H1A	109.5
Cl3—Sn1—Cl2	90.81 (2)	C2—N1—H1B	109.5
Cl3 <sup>i</sup> —Sn1—Cl2	89.19 (2)	H1A—N1—H1B	109.5
Cl1—Sn1—Cl2	88.94 (2)	C2—N1—H1C	109.5
Cl1 <sup>i</sup> —Sn1—Cl2	91.06 (2)	H1A—N1—H1C	109.5
Cl3—Sn1—Cl2 <sup>i</sup>	89.19 (2)	H1B—N1—H1C	109.5
Cl3 <sup>i</sup> —Sn1—Cl2 <sup>i</sup>	90.81 (2)	N1—C2—C3	113.2 (2)
Cl1—Sn1—Cl2 <sup>i</sup>	91.06 (2)	N1—C2—H2A	108.9
Cl1 <sup>i</sup> —Sn1—Cl2 <sup>i</sup>	88.94 (2)	C3—C2—H2A	108.9
Cl2—Sn1—Cl2 <sup>i</sup>	180	N1—C2—H2B	108.9
C5—N4—C3	113.62 (19)	C3—C2—H2B	108.9
C5—N4—H4A	108.8	H2A—C2—H2B	107.8
C3—N4—H4A	108.8	N4—C3—C2	114.31 (19)
C5—N4—H4B	108.8	N4—C3—H3A	108.7
C3—N4—H4B	108.8	C2—C3—H3A	108.7
H4A—N4—H4B	107.7	N4—C3—H3B	108.7
N4—C5—C5 <sup>ii</sup>	110.3 (3)	C2—C3—H3B	108.7
N4—C5—H5A	109.6	H3A—C3—H3B	107.6

C3—N4—C5—C5 <sup>ii</sup>	174.8 (3)	N1—C2—C3—N4	81.1 (3)
C5—N4—C3—C2	66.8 (3)		

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

#### Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1 <i>A</i> ...C14	0.89	2.30	3.172 (2)	167
N1—H1 <i>B</i> ...O1 <i>W</i>	0.89	2.09	2.980 (4)	179
N1—H1 <i>C</i> ...C11 <sup>iii</sup>	0.89	2.75	3.255 (3)	117
N1—H1 <i>C</i> ...O1 <i>W</i> <sup>iv</sup>	0.89	2.25	3.037 (4)	147
O1 <i>W</i> —H1 <i>W</i> ...C14 <sup>v</sup>	0.75 (4)	2.60 (5)	3.281 (3)	151 (4)
O1 <i>W</i> —H2 <i>W</i> ...C12 <sup>iii</sup>	0.72 (5)	2.82 (5)	3.422 (3)	144 (4)
N4—H4 <i>A</i> ...C12 <sup>iv</sup>	0.90	2.50	3.2225 (19)	138
N4—H4 <i>A</i> ...C11 <sup>vi</sup>	0.90	2.75	3.452 (2)	136
N4—H4 <i>B</i> ...C14	0.90	2.13	3.026 (2)	173
C5—H5 <i>B</i> ...C11 <sup>vii</sup>	0.97	2.76	3.445 (3)	128

Symmetry codes: (iii)  $x-1, -y+3/2, z-1/2$ ; (iv)  $x, -y+3/2, z+1/2$ ; (v)  $-x, -y+1, -z$ ; (vi)  $-x+1, y-1/2, -z+3/2$ ; (vii)  $x, -y+3/2, z-1/2$ .

### 1,4-Bis(2-ammonioethyl)piperazin-1,4-dium hexachloridostannate(IV) dichloride dihydrate (II)

#### Crystal data

(C<sub>8</sub>H<sub>24</sub>N<sub>4</sub>)[SnCl<sub>6</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O

*M<sub>r</sub>* = 614.65

Triclinic, *P*1̄

Hall symbol: -P 1

*a* = 7.0856 (2) Å

*b* = 7.3269 (2) Å

*c* = 12.1624 (4) Å

$\alpha$  = 93.614 (2)°

$\beta$  = 101.357 (1)°

$\gamma$  = 117.021 (2)°

*V* = 543.01 (3) Å<sup>3</sup>

*Z* = 1

*F*(000) = 306

*D<sub>x</sub>* = 1.88 Mg m<sup>-3</sup>

Mo *K*α radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 5436 reflections

$\theta$  = 2.9–27.5°

$\mu$  = 2.17 mm<sup>-1</sup>

*T* = 295 K

Cube, colorless

0.13 × 0.12 × 0.11 mm

#### Data collection

Nonius KappaCCD

diffractometer

Radiation source: Enraf Nonius FR590

Graphite monochromator

Detector resolution: 9 pixels mm<sup>-1</sup>

CCD rotation images, thick slices scans

Absorption correction: multi-scan

(SADABS; Krause et al., 2015)

*T<sub>min</sub>* = 0.745, *T<sub>max</sub>* = 0.893

4329 measured reflections

2494 independent reflections

2319 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.014

$\theta_{\max}$  = 27.5°,  $\theta_{\min}$  = 3.2°

*h* = -9→9

*k* = -9→9

*l* = -15→15

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.025

*wR* (*F*<sup>2</sup>) = 0.064

*S* = 1.13

2494 reflections

117 parameters

2 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

$w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 0.3256P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.61 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.65 \text{ e } \text{Å}^{-3}$   
 Extinction correction: SHELXL,  
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.033 (2)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 ( $\text{Å}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Sn1	0.5	0.5	0	0.02689 (10)
Cl3	0.78922 (11)	0.66433 (10)	0.17479 (5)	0.04033 (16)
Cl4	0.17862 (10)	0.75981 (9)	0.44661 (6)	0.03755 (16)
Cl1	0.30602 (10)	0.66732 (10)	0.06748 (5)	0.03706 (15)
Cl2	0.31206 (12)	0.19729 (9)	0.08532 (6)	0.04023 (16)
N4	0.2782 (3)	0.3944 (3)	0.42328 (16)	0.0239 (4)
H4	0.238 (5)	0.484 (5)	0.440 (2)	0.036*
C3	0.0936 (4)	0.2192 (3)	0.33497 (19)	0.0269 (5)
H3A	-0.0176	0.1302	0.3709	0.032*
H3B	0.1481	0.1361	0.3005	0.032*
O1W	0.5368 (4)	1.0237 (5)	0.3102 (2)	0.0736 (8)
H1W	0.579 (9)	1.068 (8)	0.3794 (19)	0.11*
H2W	0.404 (4)	0.939 (7)	0.297 (5)	0.11*
N1	-0.1969 (4)	0.1317 (3)	0.16070 (19)	0.0392 (5)
H1A	-0.1568	0.0426	0.1338	0.059*
H1B	-0.2451	0.1822	0.1035	0.059*
H1C	-0.3032	0.0662	0.195	0.059*
C6	0.6631 (4)	0.6818 (3)	0.4703 (2)	0.0275 (5)
H6A	0.7909	0.7482	0.4404	0.033*
H6B	0.6187	0.7849	0.4884	0.033*
C2	-0.0067 (4)	0.3044 (4)	0.2435 (2)	0.0314 (5)
H2A	-0.0531	0.3943	0.2786	0.038*
H2B	0.1021	0.3864	0.2044	0.038*
C5	0.4795 (4)	0.5058 (4)	0.3805 (2)	0.0284 (5)
H5A	0.4439	0.561	0.3136	0.034*
H5B	0.5277	0.4078	0.3582	0.034*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Sn1	0.03243 (14)	0.02481 (13)	0.02285 (14)	0.01475 (10)	0.00329 (9)	0.00328 (8)
Cl3	0.0426 (3)	0.0413 (3)	0.0303 (3)	0.0212 (3)	-0.0060 (3)	-0.0003 (3)
Cl4	0.0368 (3)	0.0320 (3)	0.0449 (4)	0.0191 (3)	0.0078 (3)	0.0000 (3)
Cl1	0.0443 (3)	0.0386 (3)	0.0376 (3)	0.0264 (3)	0.0129 (3)	0.0076 (3)
Cl2	0.0553 (4)	0.0302 (3)	0.0372 (3)	0.0189 (3)	0.0180 (3)	0.0115 (2)
N4	0.0235 (9)	0.0253 (9)	0.0233 (9)	0.0133 (7)	0.0031 (7)	0.0029 (7)
C3	0.0272 (10)	0.0248 (10)	0.0255 (11)	0.0120 (9)	0.0016 (9)	0.0030 (8)
O1W	0.0596 (15)	0.087 (2)	0.0444 (14)	0.0113 (14)	0.0113 (12)	0.0132 (14)
N1	0.0456 (12)	0.0386 (12)	0.0278 (11)	0.0211 (10)	-0.0039 (9)	0.0011 (9)
C6	0.0258 (10)	0.0277 (11)	0.0275 (11)	0.0114 (9)	0.0058 (9)	0.0100 (9)
C2	0.0314 (11)	0.0276 (11)	0.0281 (12)	0.0116 (9)	-0.0007 (9)	0.0035 (9)
C5	0.0271 (11)	0.0342 (12)	0.0242 (11)	0.0146 (9)	0.0070 (9)	0.0072 (9)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Sn1—Cl3	2.4265 (6)	O1W—H2W	0.836 (19)
Sn1—Cl3 <sup>i</sup>	2.4265 (6)	N1—C2	1.479 (3)
Sn1—Cl1 <sup>i</sup>	2.4319 (6)	N1—H1A	0.89
Sn1—Cl1	2.4319 (6)	N1—H1B	0.89
Sn1—Cl2	2.4331 (6)	N1—H1C	0.89
Sn1—Cl2 <sup>i</sup>	2.4331 (6)	C6—N4 <sup>ii</sup>	1.500 (3)
N4—C6 <sup>ii</sup>	1.500 (3)	C6—C5	1.512 (3)
N4—C5	1.503 (3)	C6—H6A	0.97
N4—C3	1.503 (3)	C6—H6B	0.97
N4—H4	0.85 (3)	C2—H2A	0.97
C3—C2	1.520 (3)	C2—H2B	0.97
C3—H3A	0.97	C5—H5A	0.97
C3—H3B	0.97	C5—H5B	0.97
O1W—H1W	0.826 (19)		
Cl3—Sn1—Cl3 <sup>i</sup>	180	H3A—C3—H3B	108.1
Cl3—Sn1—Cl1 <sup>i</sup>	90.31 (2)	H1W—O1W—H2W	106 (5)
Cl3 <sup>i</sup> —Sn1—Cl1 <sup>i</sup>	89.69 (2)	C2—N1—H1A	109.5
Cl3—Sn1—Cl1	89.69 (2)	C2—N1—H1B	109.5
Cl3 <sup>i</sup> —Sn1—Cl1	90.31 (2)	H1A—N1—H1B	109.5
Cl1 <sup>i</sup> —Sn1—Cl1	180.00 (3)	C2—N1—H1C	109.5
Cl3—Sn1—Cl2	90.42 (2)	H1A—N1—H1C	109.5
Cl3 <sup>i</sup> —Sn1—Cl2	89.58 (2)	H1B—N1—H1C	109.5
Cl1 <sup>i</sup> —Sn1—Cl2	88.55 (2)	N4 <sup>ii</sup> —C6—C5	111.57 (18)
Cl1—Sn1—Cl2	91.45 (2)	N4 <sup>ii</sup> —C6—H6A	109.3
Cl3—Sn1—Cl2 <sup>i</sup>	89.58 (2)	C5—C6—H6A	109.3
Cl3 <sup>i</sup> —Sn1—Cl2 <sup>i</sup>	90.42 (2)	N4 <sup>ii</sup> —C6—H6B	109.3
Cl1 <sup>i</sup> —Sn1—Cl2 <sup>i</sup>	91.45 (2)	C5—C6—H6B	109.3
Cl1—Sn1—Cl2 <sup>i</sup>	88.55 (2)	H6A—C6—H6B	108
Cl2—Sn1—Cl2 <sup>i</sup>	180	N1—C2—C3	110.21 (19)

C6 <sup>ii</sup> —N4—C5	109.02 (17)	N1—C2—H2A	109.6
C6 <sup>ii</sup> —N4—C3	111.27 (17)	C3—C2—H2A	109.6
C5—N4—C3	112.28 (18)	N1—C2—H2B	109.6
C6 <sup>ii</sup> —N4—H4	109 (2)	C3—C2—H2B	109.6
C5—N4—H4	107 (2)	H2A—C2—H2B	108.1
C3—N4—H4	109 (2)	N4—C5—C6	111.52 (19)
N4—C3—C2	110.33 (18)	N4—C5—H5A	109.3
N4—C3—H3A	109.6	C6—C5—H5A	109.3
C2—C3—H3A	109.6	N4—C5—H5B	109.3
N4—C3—H3B	109.6	C6—C5—H5B	109.3
C2—C3—H3B	109.6	H5A—C5—H5B	108
C6 <sup>ii</sup> —N4—C3—C2	163.67 (19)	C6 <sup>ii</sup> —N4—C5—C6	-56.4 (3)
C5—N4—C3—C2	-73.8 (2)	C3—N4—C5—C6	179.86 (18)
N4—C3—C2—N1	-176.51 (19)	N4 <sup>ii</sup> —C6—C5—N4	57.8 (3)

Symmetry codes: (i)  $-x+1, -y+1, -z$ ; (ii)  $-x+1, -y+1, -z+1$ .

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ Cl3 <sup>iii</sup>	0.89	2.71	3.397 (2)	134
N1—H1A $\cdots$ Cl2 <sup>iv</sup>	0.89	2.81	3.431 (2)	128
N1—H1B $\cdots$ Cl1 <sup>v</sup>	0.89	2.47	3.343 (2)	167
N1—H1C $\cdots$ O1W <sup>iii</sup>	0.89	1.92	2.769 (4)	158
O1W—H1W $\cdots$ Cl4 <sup>vi</sup>	0.83 (2)	2.30 (3)	3.079 (3)	158 (6)
O1W—H2W $\cdots$ Cl4	0.83 (4)	2.67 (5)	3.246 (3)	128 (5)
N4—H4 $\cdots$ Cl4	0.85 (4)	2.24 (4)	3.073 (2)	164 (3)
C2—H2B $\cdots$ Cl1	0.97	2.79	3.715 (3)	160
C6—H6A $\cdots$ Cl4 <sup>vii</sup>	0.97	2.70	3.506 (3)	141

Symmetry codes: (iii)  $x-1, y-1, z$ ; (iv)  $-x, -y, -z$ ; (v)  $-x, -y+1, -z$ ; (vi)  $-x+1, -y+2, -z+1$ ; (vii)  $x+1, y, z$ .