

Bis(pyrrolidinium) hexachloridostannate: a redetermination

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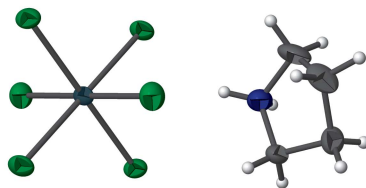
Keywords: crystal structure; pyrrolidinium; hexachlorostannate; ring conformation; disorder.

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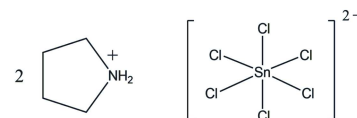
Structural data: full structural data are available from iucrdata.iucr.org

The crystal structure of the title compound, $(C_4H_{10}N)_2[SnCl_6]$, has been redetermined at 180 K. All atoms were located with higher precision than the previous structure determined at room temperature [Ishida *et al.* (2000). *J Mol. Struct.* **524**, 95–103]. In the crystal, the Sn^{IV} atom is located on a special position of site symmetry $2/m$ and is coordinated by six Cl atoms in a pseudo-octahedral geometry. Of the six Cl atoms, two equivalent axial atoms lie on the mirror plane [$Sn-Cl = 2.4281(6) \text{ \AA}$] and the other four equivalent equatorial atoms lie on general positions [$Sn-Cl = 2.4285(4) \text{ \AA}$]. The N atom of the pyrrolidinium cation lies on a mirror plane and the other atoms of the cation are disordered over two sites with respect to the mirror plane. Each component of the disordered five-membered rings adopts a twist conformation. The cations and anions are connected *via* $N-H \cdots Cl$ hydrogen bonds, forming a tape-like structure propagating along [010].

3D view



Chemical scheme



Structure description

Previously, we have reported structural phase transitions of three bis(pyrrolidinium) hexachlorometalates, namely, $2C_4H_8NH_2^+ \cdot MCl_6^{2-}$ ($M = Sn, Te, Pt$), by using ^{35}Cl nuclear quadrupole resonance (NQR) and differential scanning calorimetry (DSC). The transitions occur at 150, 159 and 134 K for the stannate, tellurate and platinate, respectively, and their crystal structures at room temperature have been determined by single-crystal X-ray diffraction (Ishida *et al.*, 2000). They are isotypic with each other, belonging to the space group $C2/m$. The pyrrolidinium cation in these crystals are expected to be rather freely packed because of the large free volume created by the bulky MCl_6^{2-} anion. The ring conformation of the pseudo-free cation was, however, not determined precisely at room temperature owing to large thermal motion, including disordering of the cation. In the present study, we have redetermined the crystal structure of the title compound at a

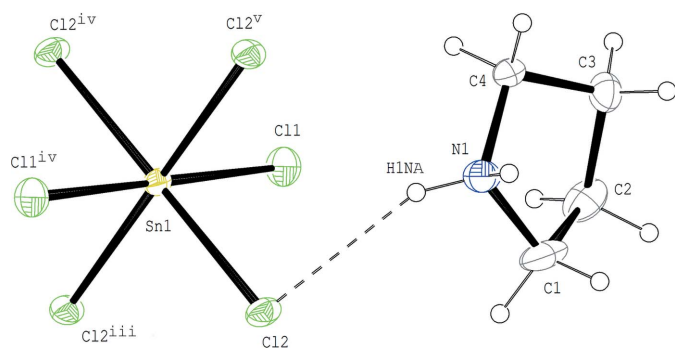


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The N–H···Cl hydrogen bond is shown as a dashed line (Table 1). Only one component is shown for the disordered cation. [Symmetry codes: (iii) $x, -y + 1, z$; (iv) $-x + 1, -y + 1, -z$; (v) $-x + 1, y, -z$.]

low temperature (180 K) in the high-temperature phase, in order to obtain precise information on the conformation of the cation and intermolecular interactions in the crystal.

A search of the Cambridge Structural Database (Version 5.39, last update August 2018; Groom *et al.*, 2016) gave 72 hits for salts of pyrrolidinium ion. The salt of the pyrrolidinium ion with a discrete MX_6 type anion (M = metal X = halogen) other than $2C_4H_{10}N^+ \cdot MCl_6^{2-}$ (M = Sn, Te, Pt) was reported for $C_4H_{10}N^+ \cdot SbCl_6^-$ (Jakubas *et al.*, 2005), in which the cation ring adopts a twist form at 300 K (CSD refcode XAKWEM) but a

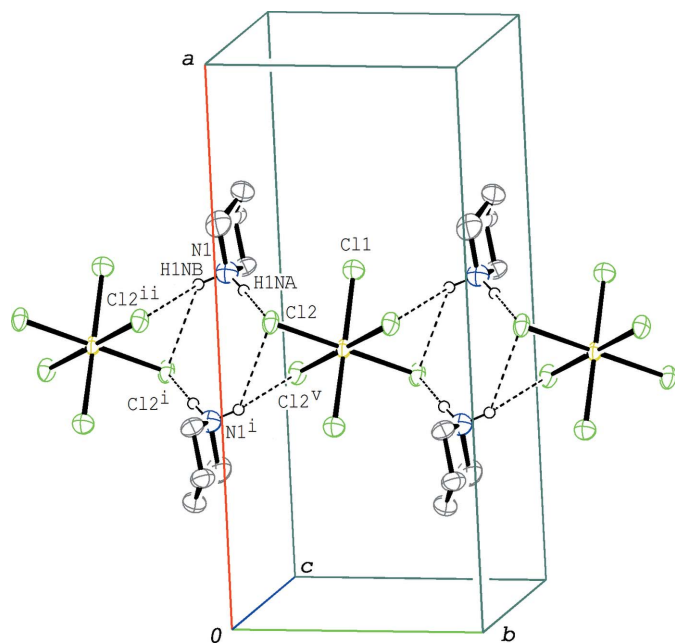


Figure 2
A partial packing diagram of the title compound, showing the tape-like structure formed by N–H···Cl hydrogen bonds (dashed lines; see Table 1). Only one component is shown for the disordered cation. Displacement ellipsoids are drawn at the 50% probability level and H atoms, except those of the NH_2 group, have been omitted. [Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $x, -y, z$; (v) $-x + 1, y, -z$.]

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1NA \cdots Cl2$	0.88 (5)	2.54 (5)	3.365 (2)	156 (5)
$N1-H1NB \cdots Cl2^i$	0.89 (4)	2.81 (6)	3.472 (2)	133 (5)
$N1-H1NB \cdots Cl2^{ii}$	0.89 (4)	2.77 (5)	3.365 (2)	126 (4)

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

flat form at 340 K (XAKWEM01) probably due to an averaging of the disordered ring. Although the pyrrolidinium ion is stable in the twist on C2–C3 form in an isolated system (Ishida, 2000), different conformations of the cation are observed in crystals, for example, an N-envelope conformation in $C_4H_{10}N^+ \cdot Cl^-$ (EHACUM; Giglmeier *et al.*, 2009) and C-envelope conformations in $C_{18}H_{16}OSi \cdot C_4H_{10}N^+ \cdot C_2H_3O_2^-$ (AJIHUY; Bauer & Strohmman, 2015) and $C_4H_{10}N^+ \cdot C_6BrF_4O^-$ (BIYFUM; Takemura *et al.*, 2014).

In the title compound, Fig. 1, the Sn^{IV} atom in the $SnCl_6^{2-}$ anion is located on a special position of site symmetry $2/m$ and is coordinated by six Cl atoms in a pseudo-octahedral geometry. Of the six Cl atoms, two Cl atoms (C11 and C12) are crystallographically independent; two equivalent axial Cl atoms lie on a mirror plane and four equivalent equatorial Cl atoms lie on general positions. The Sn–Cl bond lengths are experimentally equivalent [$Sn1-Cl1 = 2.4281(6) \text{\AA}$ and $Sn1-Cl2 = 2.4285(4) \text{\AA}$]. The N atom of the pyrrolidinium cation lies on a mirror plane and the other atoms of the cation are disordered over two sites about the mirror plane with an occupancy ratio of 0.5:0.5. The puckering parameters [$q_2 = 0.424(11) \text{\AA}$ and $\varphi_2 = 89.2(19)^\circ$] and the torsion angles of the five-membered ring show that the cation adopts a conformation close to the twist on C2–C3 form, as expected from the theoretical calculations for an isolated cation (Ishida, 2000).

In the crystal, the NH_2 group of the cation is hydrogen-bonded to the equatorial Cl atoms of the neighbouring anions ($N1-H1NA \cdots Cl2$, $N1-H1NB \cdots Cl2^i$ and $N1-$

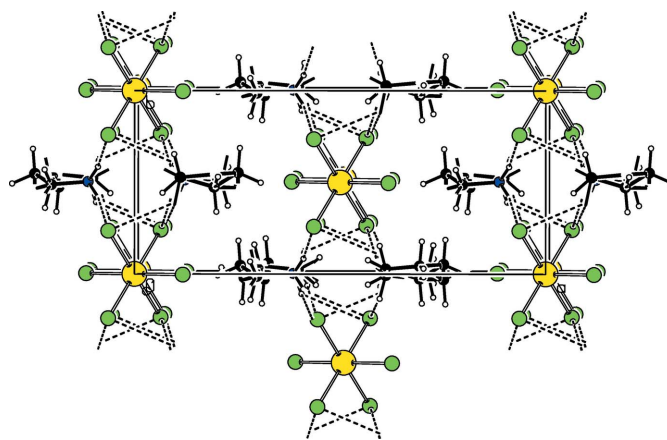


Figure 3
A view along the c axis of the crystal packing of the title compound. The N–H···Cl hydrogen bonds (Table 1) are shown as dashed lines. Only one component of the disordered cation is shown.

Table 2
Experimental details.

Crystal data	
Chemical formula	(C ₄ H ₁₀ N) ₂ [SnCl ₆]
<i>M_r</i>	475.67
Crystal system, space group	Monoclinic, <i>C2/m</i>
Temperature (K)	180
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.3784 (11), 7.3134 (3), 7.1566 (4)
β (°)	91.205 (2)
<i>V</i> (Å ³)	857.04 (8)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.41
Crystal size (mm)	0.20 × 0.20 × 0.10
Data collection	
Diffractometer	Rigaku R-Axis RAPIDII
Absorption correction	Multi-scan (<i>ABSCOR</i> ; Higashi, 1995)
<i>T</i> _{min} , <i>T</i> _{max}	0.579, 0.786
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	5281, 1343, 1308
<i>R</i> _{int}	0.038
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.704
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.024, 0.057, 1.09
No. of reflections	1343
No. of parameters	68
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.54, -1.10

Computer programs: *RAPID-AUTO* (Rigaku, 2006), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *CrystalStructure* (Rigaku, 2018) and *PLATON* (Spek, 2009).

H1NB \cdots Cl2ⁱⁱ; symmetry codes as in Table 1), forming a tape-like structure along the *b*-axis direction (Fig. 2). The anion is surrounded by six cations, four of which are linked to the anions *via* the N—H \cdots Cl hydrogen bonds (Fig. 3).

Synthesis and crystallization

The title compound was prepared by adding pyrrolidine to a hydrochloric acid solution of SnCl₄ according to the method described previously (Ishida *et al.*, 2000). Single crystals suitable for X-ray diffraction were obtained from a concentrated hydrochloric acid solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2018). 3, x181397 [https://doi.org/10.1107/S2414314618013974]

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Crystal data

(C₄H₁₀N)₂[SnCl₆]
M_r = 475.67
 Monoclinic, *C2/m*
a = 16.3784 (11) Å
b = 7.3134 (3) Å
c = 7.1566 (4) Å
 β = 91.205 (2)°
V = 857.04 (8) Å³
Z = 2

F(000) = 468.00
D_x = 1.843 Mg m⁻³
 Mo *K*α radiation, λ = 0.71075 Å
 Cell parameters from 5181 reflections
 θ = 3.1–30.0°
 μ = 2.41 mm⁻¹
T = 180 K
 Platelet, colorless
 0.20 × 0.20 × 0.10 mm

Data collection

Rigaku R-AXIS RAPIDII
 diffractometer
 Detector resolution: 10.000 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
T_{min} = 0.579, *T_{max}* = 0.786
 5281 measured reflections

1343 independent reflections
 1308 reflections with *I* > 2σ(*I*)
R_{int} = 0.038
 θ_{\max} = 30.0°, θ_{\min} = 3.1°
h = -22→22
k = -10→9
l = -10→10

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.024
wR(*F*²) = 0.057
S = 1.09
 1343 reflections
 68 parameters
 2 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.3195P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.54 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.10 \text{ e \AA}^{-3}$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Sn1	0.500000	0.500000	0.000000	0.02448 (8)	
Cl1	0.61941 (4)	0.500000	0.20690 (9)	0.03911 (14)	
Cl2	0.56208 (3)	0.26144 (5)	-0.18554 (6)	0.03335 (10)	
N1	0.61485 (15)	0.000000	0.1846 (3)	0.0378 (5)	
H1NA	0.590 (4)	0.082 (6)	0.113 (7)	0.057*	0.5
H1NB	0.595 (4)	-0.111 (5)	0.163 (7)	0.057*	0.5
C1	0.7040 (2)	-0.015 (5)	0.1454 (6)	0.054 (3)	0.5
H1A	0.718653	-0.141991	0.112102	0.065*	0.5
H1B	0.719081	0.067232	0.041717	0.065*	0.5
C2	0.7455 (2)	0.0412 (6)	0.3229 (7)	0.0512 (12)	0.5
H2A	0.750038	0.175930	0.331790	0.061*	0.5
H2B	0.800714	-0.013262	0.334683	0.061*	0.5
C3	0.6886 (2)	-0.0348 (6)	0.4717 (5)	0.0419 (13)	0.5
H3A	0.694280	-0.169065	0.484205	0.050*	0.5
H3B	0.699197	0.023171	0.594843	0.050*	0.5
C4	0.60557 (18)	0.017 (3)	0.3925 (4)	0.034 (3)	0.5
H4A	0.562866	-0.066758	0.437619	0.041*	0.5
H4B	0.591198	0.143984	0.427417	0.041*	0.5

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.02747 (11)	0.01710 (11)	0.02918 (12)	0.000	0.00770 (7)	0.000
Cl1	0.0362 (3)	0.0386 (3)	0.0423 (3)	0.000	-0.0047 (2)	0.000
Cl2	0.0398 (2)	0.02416 (18)	0.0366 (2)	0.00185 (14)	0.01405 (15)	-0.00506 (14)
N1	0.0375 (11)	0.0426 (12)	0.0334 (10)	0.000	0.0050 (8)	0.000
C1	0.0469 (16)	0.059 (10)	0.0573 (18)	0.002 (4)	0.0289 (14)	-0.009 (6)
C2	0.0279 (14)	0.047 (3)	0.079 (3)	-0.0078 (14)	0.0107 (15)	-0.0076 (19)
C3	0.0323 (14)	0.044 (4)	0.0490 (16)	0.0022 (14)	-0.0033 (12)	0.0092 (16)
C4	0.0279 (11)	0.044 (8)	0.0313 (10)	0.006 (3)	0.0072 (8)	0.004 (2)

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

Sn1—Cl1 ⁱ	2.4281 (6)	C1—H1A	0.9900
Sn1—Cl1	2.4281 (6)	C1—H1B	0.9900
Sn1—Cl2	2.4285 (4)	C2—C3	1.534 (5)
Sn1—Cl2 ⁱ	2.4285 (4)	C2—H2A	0.9900
Sn1—Cl2 ⁱⁱ	2.4285 (4)	C2—H2B	0.9900
Sn1—Cl2 ⁱⁱⁱ	2.4285 (4)	C3—C4	1.512 (8)
N1—C1	1.497 (5)	C3—H3A	0.9900
N1—C4	1.504 (4)	C3—H3B	0.9900
N1—H1NA	0.883 (19)	C4—H4A	0.9900
N1—H1NB	0.89 (2)	C4—H4B	0.9900
C1—C2	1.486 (12)		

C11 ⁱ —Sn1—C11	180.0	N1—C1—H1A	110.9
C11 ⁱ —Sn1—C12	90.439 (16)	C2—C1—H1B	110.9
C11—Sn1—C12	89.560 (16)	N1—C1—H1B	110.9
C11 ⁱ —Sn1—C12 ⁱ	89.561 (16)	H1A—C1—H1B	108.9
C11—Sn1—C12 ⁱ	90.440 (16)	C1—C2—C3	102.7 (7)
C12—Sn1—C12 ⁱ	180.000 (18)	C1—C2—H2A	111.2
C11 ⁱ —Sn1—C12 ⁱⁱ	89.561 (16)	C3—C2—H2A	111.2
C11—Sn1—C12 ⁱⁱ	90.440 (16)	C1—C2—H2B	111.2
C12—Sn1—C12 ⁱⁱ	88.151 (19)	C3—C2—H2B	111.2
C12 ⁱ —Sn1—C12 ⁱⁱ	91.849 (19)	H2A—C2—H2B	109.1
C11 ⁱ —Sn1—C12 ⁱⁱⁱ	90.439 (16)	C4—C3—C2	101.7 (5)
C11—Sn1—C12 ⁱⁱⁱ	89.560 (16)	C4—C3—H3A	111.4
C12—Sn1—C12 ⁱⁱⁱ	91.849 (19)	C2—C3—H3A	111.4
C12 ⁱ —Sn1—C12 ⁱⁱⁱ	88.151 (19)	C4—C3—H3B	111.4
C12 ⁱⁱ —Sn1—C12 ⁱⁱⁱ	180.000 (13)	C2—C3—H3B	111.4
C1—N1—C4	108.1 (3)	H3A—C3—H3B	109.3
C1—N1—H1NA	112 (5)	N1—C4—C3	104.0 (5)
C4—N1—H1NA	118 (4)	N1—C4—H4A	111.0
C1—N1—H1NB	105 (5)	C3—C4—H4A	111.0
C4—N1—H1NB	102 (4)	N1—C4—H4B	111.0
H1NA—N1—H1NB	110 (4)	C3—C4—H4B	111.0
C2—C1—N1	104.5 (7)	H4A—C4—H4B	109.0
C2—C1—H1A	110.9		
C4—N1—C1—C2	-14 (2)	C1—N1—C4—C3	-13 (2)
N1—C1—C2—C3	36 (2)	C2—C3—C4—N1	34.7 (13)
C1—C2—C3—C4	-43.9 (15)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1NA \cdots C12	0.88 (5)	2.54 (5)	3.365 (2)	156 (5)
N1—H1NB \cdots C12 ^{iv}	0.89 (4)	2.81 (6)	3.472 (2)	133 (5)
N1—H1NB \cdots C12 ^v	0.89 (4)	2.77 (5)	3.365 (2)	126 (4)

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