Bis(4-aminopyridinium) hexachlorido-stannate(IV) and bis(p-toluidinium) hexachloridostannate(IV)

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The crystal structures of the two organic–inorganic hybrids bis(4-aminopyridinium)hexachloridostannate(IV),$(C_5H_7N_2)_2$-$[SnCl_6]$, and bis(p-toluidinium) hexachloridostannate(IV), $(C_7H_{10}N)_2[SnCl_6]$, differ in the way their cations pack in the layered structures. The Sn atom in the 4-aminopyridinium compound lies on an inversion centre.

Comment

As part of a study of the effect of cations on the crystal structures of organic–inorganic ammonium hexachlorido-stannate(IV) hybrids, we report here two new structures with different aromatic organic ammonium cations. This type of hybrid generally exhibits a structure consisting of alternating inorganic layers, characterized by isolated octahedra of $[SnCl_6]^{2-}$ anions, and organic layers, made up of alkyl-ammonium $(C_nH_{2n+1}NH_3^+)$ or aromatic ammonium $(C_6H_5-R-NH_3^+)$ cations (Lemmerer et al., 2007; Billing et al., 2007, and references therein). The two title compounds, namely bis(4-aminopyridinium) hexachloridostannate(IV), (I), and bis(p-toluidinium) hexachloridostannate(IV), (II), differ in the hydrogen-bonding capability of their cations, with the cation in (I) able to hydrogen bond at both ends of the molecule, whereas the cation in (II) only has hydrogen-bonding capability at one end of the molecule. The two structures exhibit similarities to and differences from previously reported crystal structures of this type. The molecular geometry and numbering schemes of (I) and (II) are shown in Fig. 1.

The organic–inorganic hybrid structure of (I) has $SnCl_6$ octahedra at each of the eight vertices of the triclinic unit cell, encapsulating two 4-aminopyridinium cations in the centre of the unit cell (Fig. 2). A layered structure results, with the $SnCl_6$ octahedra forming the inorganic layer and the cations packing in the organic layer. The asymmetric unit of the inorganic part contains an Sn^{IV} atom on an inversion centre and three Cl

atoms on general positions, labelled Cl1, Cl2 and Cl3. The inversion symmetry operator generates the full octahedral coordination. The Sn—Cl bond lengths are given in Table 1 and average 2.439 (9) Å. The bond angles between trans-related Cl atoms are exactly 180° and the cis angles range from 88.78 (2) to 91.22 (2)°.
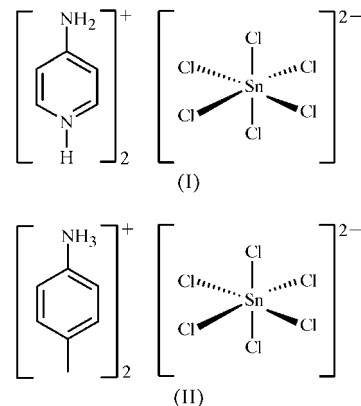
The organic part of (I) has one 4-aminopyridinum cation in the asymmetric unit. In the organic layer, these cations pack in an interdigitated fashion so that opposite ends of the cation hydrogen bond to inorganic layers. This results in a short inter-layer spacing of 8.3403 (8) Å. Adjacent cations are stacked antiparallel, with a centroid-to-centroid distance of 4.24 (1) Å. This distance is significantly greater than the value of 3.8 Å commonly used as the cut-off distance for accepted π–π interactions (Janiak, 2000). Closer contacts have been found for this cation in molecular crystals (3.473 Å; Kennedy & Kittner, 2005).
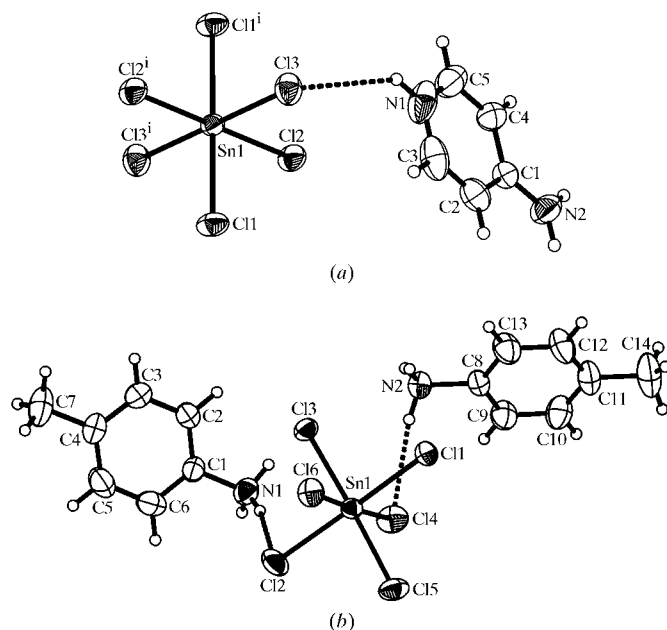

Figure 1
Views of the structures of (a) (I) and (b) (II), showing the atomic numbering schemes. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 2, -y + 2, -z$.]

The interactions between the inorganic and organic parts are dominated by N—H···Cl—Sn charge-assisted hydrogen bonds, viz. two hydrogen bonds involving atom N2 of the ammonium group, being 2.54 and 2.66 Å long, and another hydrogen bond involving atom N1 of the pyridine ring, being 2.68 Å long. In addition, there is a short-contact interaction between atoms N1 and Cl1($-x + 1$, $-y + 2$, $-z$) (2.91 Å). These interactions result in a two-dimensional hydrogen-bond network parallel to (111). Fig. 3 illustrates the various interactions and Table 2 summarizes the geometric parameters. There is also an $X—Y\cdots\pi$ short contact between the ring centroid and atom Cl1 on the SnCl$_6$ octahedra [Cl1$\cdots Cg$ = 3.910 (2) Å and Sn1—Cl1$\cdots Cg$ = 120.71 (2)°].

The packing of (II) is different from that of (I) (Fig. 4) in that it exhibits a more distinct organic layer, similar to what was observed for the previously reported hexachloridostannate(IV) hybrid structures. This is because the cations in

the inorganic layer are more offset than in (I), and thus only slightly interdigitated, with only one end of the cation interacting with a single inorganic layer via hydrogen bonds. The interlayer spacing is larger than for structure (I), with a value of 12.652 (2) Å along the b axis. The p-toluidinium cations pack antiparallel, with a centroid-to-centroid distance of 5.251 (2) Å. The asymmetric unit is roughly twice that of (I), the inorganic part consisting of a complete SnCl$_6$ octahedron, where the Sn^{IV} atom and atoms Cl1 through to Cl6 are on general positions. The six unique Sn—Cl bond lengths average 2.429 (14) Å. The bond angles between trans-related Cl atoms deviate from 180° (Table 3) and the cis angles range from 87.65 (3) to 92.04 (3)°. To balance the charge, two independent toluidinium cations are found in the asymmetric unit of the organic part.

In (II), hydrogen-bonding interactions between the Cl atoms and the ammonium group form a two-dimensional hydrogen-bonded sheet parallel to the ac plane. All six H atoms form simple hydrogen bonds, with no bifurcated geometries observed (Fig. 5 and Table 4).

In conclusion, by increasing the hydrogen-bonding capability of the cation from only one end of the cation in (II) to two opposite ends of the cation in (I), the dimensionality of the hydrogen-bonding network is not changed. However, the inorganic layer changes from only slightly interdigitated in (II) to completely interdigitated in (I), allowing both ends of the cation to hydrogen bond to inorganic layers on opposite sides of the cation. This behaviour illustrates that the hydrogen-bonding capability of the cation can be utilized to give some
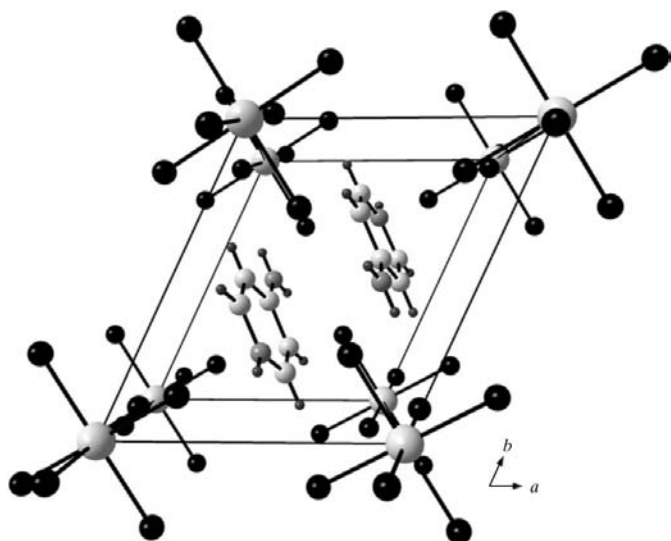

Figure 2
A packing diagram of (I), viewed in perspective along the c axis.
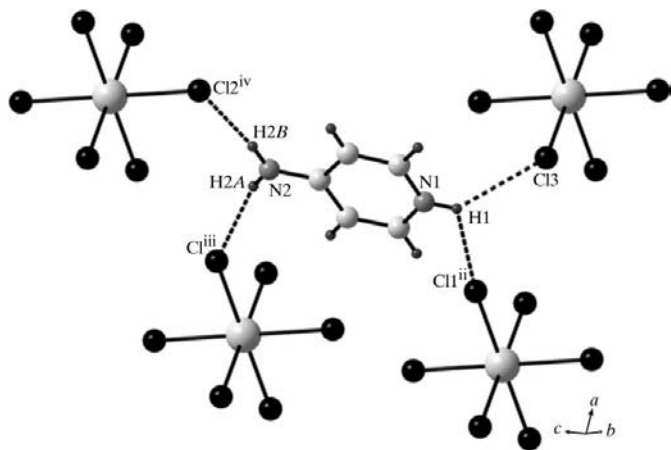

Figure 3
A magnified view of the various N—H···Cl hydrogen bonds and short contacts (dashed lines) in (I). [Symmetry codes: (ii) $-x + 1$, $-y + 2$, $-z$; (iii) $-x + 1$, $-y + 2$, $-z + 1$; (iv) $-x + 2$, $-y + 1$, $-z + 1$.]
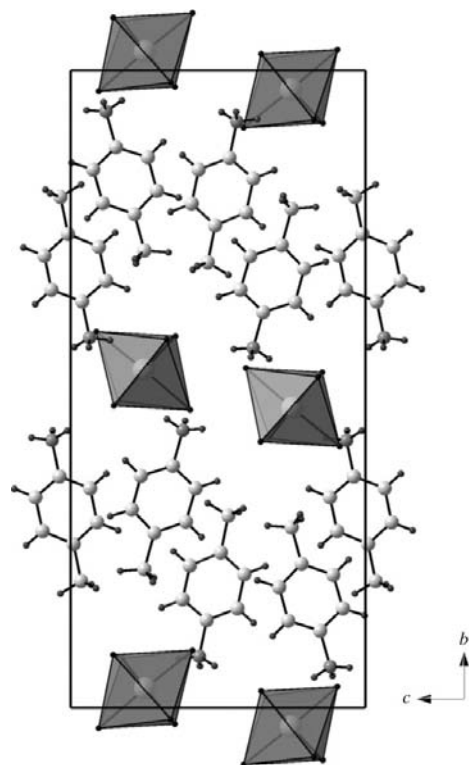

Figure 4
A packing diagram of (II), viewed along the a axis.

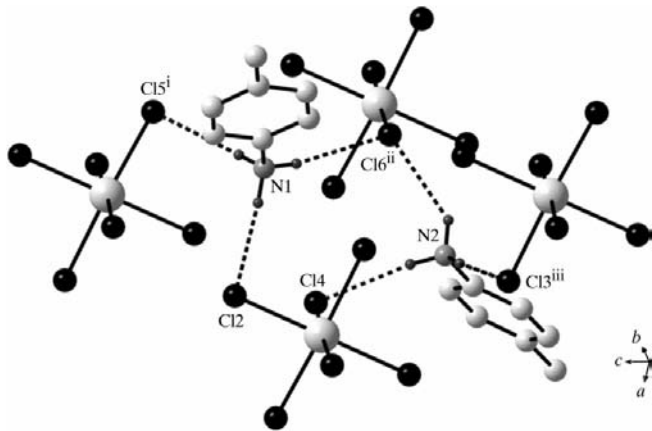control over the degree of overlap or interdigitation in the organic layer of this type of organic–inorganic hybrid.

Figure 5
The N—H···Cl hydrogen bonds between the two toluidinium cations [cat1 (N1) and cat2 (N2)] in (II). [Symmetry codes: (i) $-x + 1$, $-y + 1$, $-z + 1$; (ii) $x - 1$, y, z; (iii) $-x + 1$, $-y + 1$, $-z$.]

Experimental

For the preparation of (I), 4-aminopyridinium chloride was prepared by the dropwise addition of excess HCl (0.52 ml, 37%, Aldrich) to a solution of 4-aminopyridine (0.874 g, 98%, Aldrich) in 15 ml of chloroform (99%, Saarchem). The resulting precipitate of 4-amino-pyridinium chloride was filtered off. Compound (I) was crystallized from a solution of 4-aminopyridinium (0.421 g) and $SnCl_4 \cdot 5H_2O$ (0.571 g, 98%, Aldrich) in 45 ml of water, at room temperature, over a period of five weeks. For the preparation of (II), p-toluidinium chloride was precipitated by adding excess HCl (0.48 ml, 37%, Aldrich) dropwise to a solution of p-toluidine (0.994 g, 99%, Aldrich) in 40 ml of chloroform (99%, Saarchem). The precipitate was filtered off. p-Toluidinium chloride (0.396 g) and $SnCl_4 \cdot 5H_2O$ (0.502 g, 98%, Aldrich) were dissolved in 40 ml of water. Compound (II) crystallized from the solution, at room temperature, over a period of four weeks.

Compound (I)

Crystal data

$(C_5H_7N_2)_2[SnCl_6]$	$\gamma = 65.225\ (5)°$
$M_r = 521.64$	$V = 454.96\ (7)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 7.2248\ (6)$ Å	Mo $K\alpha$ radiation
$b = 8.3273\ (7)$ Å	$\mu = 2.28$ mm^{-1}
$c = 8.3403\ (8)$ Å	$T = 293\ (2)$ K
$\alpha = 89.100\ (6)°$	$0.34 \times 0.26 \times 0.18$ mm
$\beta = 87.002\ (6)°$	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	6423 measured reflections
	2197 independent reflections
Absorption correction: integration ($XPREP$; Bruker, 1999)	2109 reflections with $I > 2\sigma(I)$
$T_{min} = 0.518$, $T_{max} = 0.690$	$R_{int} = 0.074$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	98 parameters
$wR(F^2) = 0.051$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{max} = 0.41$ e Å^{-3}
2197 reflections	$\Delta\rho_{min} = -0.62$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

Cl1—Sn1	2.4317 (5)	Sn1—Cl1^i	2.4317 (5)
Cl2—Sn1	2.4351 (5)	Sn1—Cl2^i	2.4351 (6)
Cl3—Sn1	2.4487 (5)	Sn1—Cl3^i	2.4487 (5)

Symmetry code: (i) $-x + 2$, $-y + 2$, $-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl3	0.86	2.68	3.375 (3)	139
N1—H1···Cl1^{ii}	0.86	2.91	3.3602 (19)	115
N2—H2A···Cl1^{iii}	0.86	2.66	3.491 (2)	164
N2—H2B···Cl2^{iv}	0.86	2.54	3.388 (2)	171

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

Compound (II)

Crystal data

$(C_7H_{10}N)_2[SnCl_6]$	$V = 2104.4\ (3)$ Å^3
$M_r = 547.71$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 7.1166\ (5)$ Å	$\mu = 1.98$ mm^{-1}
$b = 25.304\ (2)$ Å	$T = 293\ (2)$ K
$c = 11.6862\ (9)$ Å	$0.4 \times 0.16 \times 0.07$ mm
$\beta = 90.239\ (4)°$	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	15513 measured reflections
	5075 independent reflections
Absorption correction: integration ($XPREP$; Bruker, 1999)	4041 reflections with $I > 2\sigma(I)$
$T_{min} = 0.583$, $T_{max} = 0.879$	$R_{int} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	212 parameters
$wR(F^2) = 0.082$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{max} = 0.65$ e Å^{-3}
5075 reflections	$\Delta\rho_{min} = -0.85$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Cl1—Sn1	2.4173 (8)	Cl4—Sn1	2.4217 (8)
Cl2—Sn1	2.4282 (8)	Cl5—Sn1	2.4158 (8)
Cl3—Sn1	2.4369 (7)	Cl6—Sn1	2.4510 (8)
Cl1—Sn1—Cl2	177.61 (3)	Cl4—Sn1—Cl6	177.13 (3)
Cl5—Sn1—Cl3	177.34 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl6^{ii}	0.89	2.51	3.387 (3)	167
N1—H1B···Cl5^i	0.89	2.55	3.416 (3)	164
N1—H1C···Cl2	0.89	2.59	3.456 (3)	165
N2—H2A···Cl3^{iii}	0.89	2.46	3.351 (3)	174
N2—H2B···Cl4	0.89	2.53	3.411 (3)	172
N2—H2C···Cl6^{ii}	0.89	2.64	3.326 (3)	134

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

metal-organic compounds

For both compounds, all H atoms were refined using a riding model, with C—H distances of either 0.93 or 0.96 Å and N—H distances of either 0.86 or 0.89 Å, and with U_{iso}(H) values of $1.2U_{eq}$(C,N) or $1.5U_{eq}$(C,N).

For both compounds, data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

References

Billing, D. G., Lemmerer, A. & Rademeyer, M. (2007). *Acta Cryst.* C**63**, m101–m104.
Brandenburg, K. (1999). *DIAMOND*. Version 2.1e. Crystal Impact GbR, Bonn, Germany.
Bruker (1998). *SMART-NT*. Version 5.050. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SAINT-Plus* (including *XPREP*). Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
Kennedy, A. R. & Kittner, M. (2005). *Acta Cryst.* E**61**, o333–o334.
Lemmerer, A., Billing, D. G. & Reisinger, S. A. (2007). *Acta Cryst.* C**63**, m97–m100.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.