

Tetrakis(anilinium) hexachlorotin(IV) dichloride

Melanie Rademeyer

School of Pure and Applied Chemistry,
University of KwaZulu-Natal, Durban 4041,
South Africa

Correspondence e-mail: rademeyerm@nu.ac.za

The crystal structure of the double salt tetrakis(anilinium) hexachlorotin(IV) dichloride, $(C_6H_8N)_4[SnCl_6]Cl_2$, exhibits alternating inorganic and organic layers parallel to the *ab* plane. In the inorganic layer, ammonium groups interact with chloride anions and isolated tilted $[SnCl_6]^{2-}$ octahedra through $N-H \cdots Cl$ hydrogen bonds.

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Key indicators

Single-crystal X-ray study

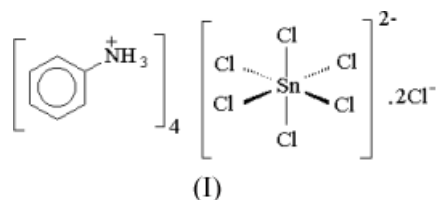
 $T = 293\text{ K}$ Mean $\sigma(C-C) = 0.006\text{ \AA}$ R factor = 0.043 wR factor = 0.104

Data-to-parameter ratio = 31.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

Organic–inorganic hybrid materials of the formula $(R-NH_3)_2SnX_4$, where $X = F, Cl, Br$ or I , exhibit interesting magnetic and electronic properties (Koutselas *et al.*, 1996; Mitzi *et al.*, 1998; Kagan *et al.*, 1999), resulting in interest in their crystal structures. However, the structural characteristics of the related organic–inorganic hybrid compounds with the formula $(R-NH_3)_2SnX_6$ have not been studied extensively. In the course of investigating compounds of this formula, the title compound, displaying an unexpected combination of anions and cations, was crystallized. Tetrakis(anilinium) hexachlorotin(IV) dichloride, (I), is a double salt of anilinium chloride and $SnCl_4$, with the formula $(C_6H_8N)_4[SnCl_6]Cl_2$. Crystal structures of these types of organic inorganic double salts have been reported for metals in the +2 oxidation state, with formulae $(R-NH_3)_3[MCl_4]Cl$ (Geiser *et al.*, 1984), $(R-NH_3)_6[MCl_6]Cl_2$ (Geselle & Fuess, 1995) and $(R-NH_3)_8[MCl_6]Cl_4$ (Tucker *et al.*, 1991), and for metals in the +3 oxidation state with formulae $(R-NH_3)_4[MCl_4]_3Cl$ (Dubois *et al.*, 1989; Martell & Zaworotko, 1991), $(R-NH_3)_2[MBr_2]Br$ (Sproul & Stucky, 1972) and $(R-NH_3)_4[MX_6]X$, where $X = Cl$ or Br (Khan & Tuck, 1981; Knop *et al.*, 1987). No crystal structure of such a material with the metal in the +4 oxidation state and a primary ammonium ion could be located in the literature. In this investigation, the structure of an organic–inorganic hybrid double salt of the formula $(R-NH_3)_4[MCl_6]Cl_2$, where M is in the +4 oxidation state, was determined.



The molecular geometry and numbering used is shown in Fig. 1. The asymmetric unit contains four anilinium cations, two chloride anions and one independent octahedral $[SnCl_6]^{2-}$ anion.

The crystal structure consists of alternating organic and inorganic layers extending parallel to the *ab* plane, and is

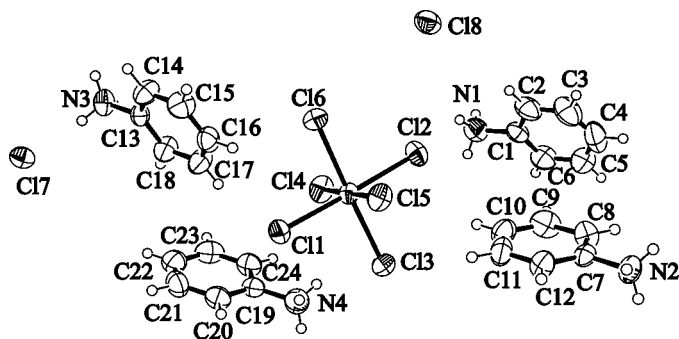


Figure 1
The molecular structure of (I), showing the atomic numbering scheme and displacement ellipsoids at the 50% probability level.

illustrated in Fig. 2. The organic layer contains the aromatic rings, and the inorganic layer comprises the ammonium groups, chloride anions and independent $[\text{SnCl}_6]^{2-}$ octahedra.

In the organic layer, the aromatic rings are not interdigitated, and are tilted relative to the ionic layer. The atoms in each of the anilinium cations are coplanar, with r.m.s deviations of 0.0067, 0.0068, 0.0064 and 0.0031 Å. The orientation of each of the crystallographically inequivalent anilinium groups relative to the inorganic layer is different (Fig. 2), with the molecular planes of the four cations tilted at angles of 84.86 (7), 77.77 (6), 80.23 (6) and 86.85 (6)° to the inorganic plane. No π - π stacking interactions are observed in the hydrocarbon layer, with all centroid-to-centroid distances in excess of 4.851 (3) Å.

In the inorganic layer, ammonium groups interact with chloride anions and $[\text{SnCl}_6]^{2-}$ octahedra *via* hydrogen bonds. Unlike structures of the type $(R-\text{NH}_3)_2\text{SnX}_4$ (Raptopoulou *et al.*, 2002), the $[\text{SnCl}_6]^{2-}$ octahedra do not share corners, but are isolated as observed in structures of the type $(R-\text{NH}_3)_2\text{SnX}_6$ (Kitahama *et al.*, 1979; Knop *et al.*, 1983; Elleuch *et al.*, 1996; Rademeyer, 2004). The octahedra are tilted relative to the *ab* plane, by an angle of 35.36 (2)°, and are slightly distorted. Sn-Cl bond lengths range from 2.4057 (10) to 2.4541 (10) Å and are listed in Table 1.

The hydrogen-bonding interactions exhibited by atoms N1, N3 and N4 are similar, and differ from the interactions displayed by atom N2. Atoms N1, N3 and N4 each form two hydrogen bonds to two independent chloride anions, and one hydrogen bond to a Cl atom in an $[\text{SnCl}_6]^{2-}$ octahedron. Atom N2 participates in four hydrogen bonds, two of which are normal hydrogen bonds involving chloride anions, and one a bifurcated hydrogen bond to two Cl atoms (Cl1 and Cl6) in an $[\text{SnCl}_6]^{2-}$ octahedron (symmetry code: $x, -y - 1, z - \frac{1}{2}$).

Each $[\text{SnCl}_6]^{2-}$ octahedron is involved in four hydrogen-bonding interactions to N atoms, but atoms Cl3 and Cl4 do not participate in any hydrogen-bond formation. Each chloride anion interacts with four hydrogen-bond donors, with atom Cl7 accepting from atoms N2, N3 and two N4 atoms, and atom Cl8 from atoms N2, N3 and two N1 atoms.

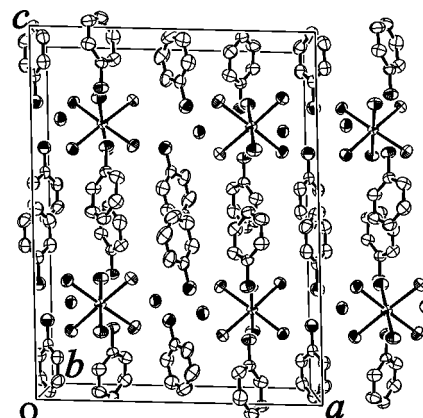


Figure 2
Packing diagram for (I), showing the layered packing (H atoms omitted).

As a result of these interactions, a hydrogen-bond network is established in which metal octahedra and chloride anions are linked through ammonium groups. This network is illustrated in Fig. 3, and hydrogen-bonding parameters are listed in Table 2.

Experimental

Anilinium chloride was prepared by the dropwise addition of concentrated hydrochloric acid (37%, Aldrich) to a solution of aniline (99%, Saarchem) in chloroform (99%, Saarchem). The precipitate was filtered off and allowed to dry. The title compound was crystallized by slow evaporation of a methanol solution of $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ (96%, Saarchem) and aniline chloride (stoichiometric ratio of 1:2), at room temperature. A needle-like light-brown crystal was selected for the X-ray diffraction study.

Crystal data

$(\text{C}_6\text{H}_8\text{N})_4[\text{SnCl}_6]\text{Cl}_2$
 $M_r = 778.83$
 Monoclinic, $P2_1/c$
 $a = 15.615$ (4) Å
 $b = 10.543$ (4) Å
 $c = 20.403$ (5) Å
 $\beta = 92.40$ (2)°
 $V = 3355.9$ (17) Å³
 $Z = 4$

$D_x = 1.541$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 185 reflections
 $\theta = 2$ -32°
 $\mu = 1.42$ mm⁻¹
 $T = 293$ (2) K
 Block, light brown
 0.50 × 0.20 × 0.20 mm

Data collection

Oxford Excalibur2 diffractometer
 ω -2 θ scans
 Absorption correction: multi-scan (Blessing, 1995)
 $T_{\min} = 0.532$, $T_{\max} = 0.757$
 30 679 measured reflections
 10 736 independent reflections

5357 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\text{max}} = 31.9^\circ$
 $h = -22 \rightarrow 22$
 $k = -12 \rightarrow 15$
 $l = -29 \rightarrow 29$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.104$
 $S = 0.92$
 10 736 reflections
 338 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0411P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.005$
 $\Delta\rho_{\text{max}} = 1.02$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.58$ e Å⁻³

Table 1
Selected interatomic distances (Å).

Sn—Cl4	2.4057 (10)	Sn—Cl5	2.4366 (10)
Sn—Cl3	2.4223 (10)	Sn—Cl6	2.4533 (10)
Sn—Cl1	2.4292 (10)	Sn—Cl2	2.4541 (10)

Table 2
Hydrogen-bonding 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>
N2—H2A...Cl7 ⁱ	0.89	2.21	3.098 (3)	175
N2—H2B...Cl6 ⁱⁱ	0.89	2.53	3.266 (3)	141
N2—H2B...Cl1 ⁱⁱ	0.89	2.82	3.538 (3)	139
N2—H2C...Cl8 ⁱⁱⁱ	0.89	2.28	3.167 (3)	173
N3—H3A...Cl2 ^{iv}	0.89	2.46	3.280 (3)	154
N3—H3B...Cl8 ^v	0.89	2.32	3.210 (3)	176
N3—H3C...Cl7	0.89	2.22	3.097 (3)	168
N1—H1C...Cl8 ^{vi}	0.89	2.26	3.148 (3)	172
N1—H1A...Cl8 ^{vii}	0.89	2.50	3.307 (3)	151
N1—H1B...Cl5 ^{vi}	0.89	2.63	3.459 (3)	156
N4—H4A...Cl7 ^{viii}	0.89	2.60	3.267 (3)	133
N4—H4B...Cl7 ^{ix}	0.89	2.51	3.313 (3)	150
N4—H4C...Cl1 ^x	0.89	2.80	3.553 (3)	143

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

All H atoms were placed in calculated positions and refined using a riding model. All H atoms were placed in calculated positions, with C—H distances of 0.93 Å and N—H distances of 0.89 Å, and were refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{parent atom})$. The maximum electron-density peak is 2.523 Å from atom N4 and 1.974 Å from Cl3.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlisCCD*; data reduction: *CrysAlisRED* (Oxford Diffraction, 2003); 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); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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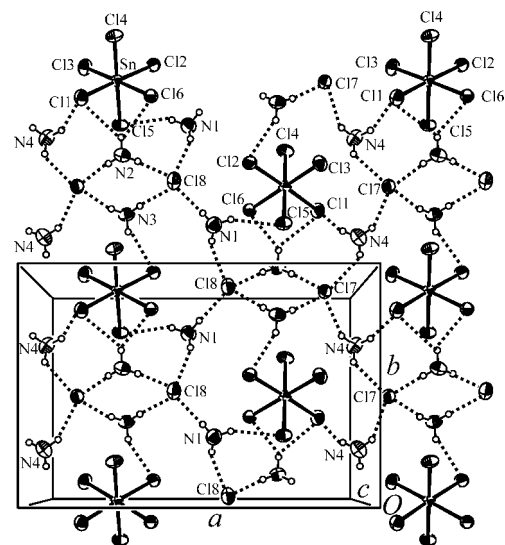


Figure 3

The hydrogen-bonding network (dashed lines) in the inorganic layer, viewed down the *c* axis.

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