Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(2-Thienylmethyl)ammonium trichlorostannate(II): a hybrid salt

Nicolas Mercier,* Antoine Seyeux, Celine Morel and Amedee Riou

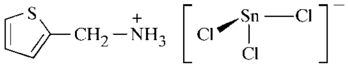
Laboratoire Ingénierie Moléculaire et Matériaux Organiques, UMR CNRS 6501, Faculté des Sciences, 2 Boulevard Lavoisier, F-49045 Angers, France
Correspondence e-mail: nicolas.mercier@univ-angers.fr

Received 17 October 2001
Accepted 4 December 2001
Online 31 January 2002

The structure of the title hybrid salt, $(C_5H_8NS)[SnCl_3]$, is built up from segregated layers of organic cations and Sn polyhedra. $[SnCl_3]^-$ groups are linked together by weak Sn···Cl interactions to form a one-dimensional polymeric chain of anions.

Comment

Organic and inorganic compounds have distinct properties and advantages, and the possibility of combining organic and inorganic components in a single hybrid compound appears very interesting. Among such hybrids, organic–inorganic perovskites are the most extensively studied group (Mitzi, 1999). These layered systems, in the simplest examples, are built up from $M^{II}[X_4^{2-}]$ (M is Pb or Sn, and X is Cl, Br or I) perovskite single layers separated either by double layers of organic monoammonium cations, *e.g.* $[R\text{–}NH_3]_2[MX_4]$, or monolayers of organic diammonium cations, *e.g.* $[H_3N\text{–}R\text{–}NH_3][MX_4]$, R being an aliphatic chain, a phenyl derivative or a tetrathiophene derivative. To date, the only reported structure containing the (2-thienylmethyl)ammonium cation, A, is that of (2-thienylmethyl)ammonium 5-hydroxy-4-methoxycarbonyl-1-(2-thienyl)-1,2,3-triazole (Murray-Rust *et al.*, 1984). We present here the structure of the second such compound, namely the title salt, $A[SnCl_3]$, (I).



(I)

The structure of (I) consists of sheets of organic cations alternating with inorganic anion layers stacked in the [010] direction (Fig. 1). At first sight, the presence of face-to-face and head-to-tail pairs of (2-thienylmethyl)ammonium cations may suggest that perovskite layers of corner-sharing divalent tin octahedra do not occur. However, recent results have shown that bilayers of these organic ammonium cations appear in the perovskite compound $A_2[PbCl_4]$ (Mercier & Riou, 2002).

In the structure of (I), isolated Sn^{II} polyhedra are present. The coordination of Sn^{II} (Table 1) consists of three short Sn—Cl bonds [2.4951 (13)–2.5837 (13) Å] and two longer weaker Sn···Cl bonds [3.4071 (17) and 3.5990 (15) Å] distributed along the axes of an octahedron, the vacancy probably being occupied by the lone pair of Sn^{II}. A valence-bond calculation, as proposed by Brown (1981), using the bond-valence parameters of Brese & O'Keeffe (1991) {calculated valence $S = \Sigma s$ with $s = \exp[(R_0 - d)/0.37]$, where d is the metal–ligand distance and R_0 is a value taken from Brese & O'Keeffe (1991) [$R_0(Sn^{II}\text{—}Cl) = 2.36$]}, suggests that the coordination of the

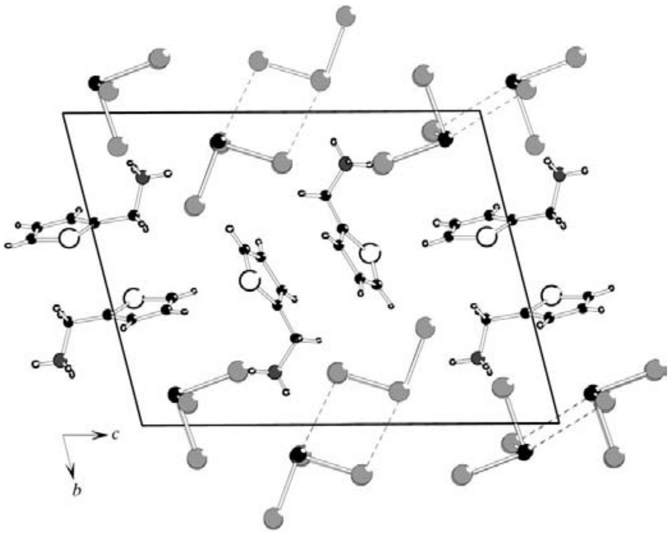


Figure 1
The structure of (I). The atoms are shown as spheres of arbitrary radii and dashed lines represent weak Sn···Cl bonds.

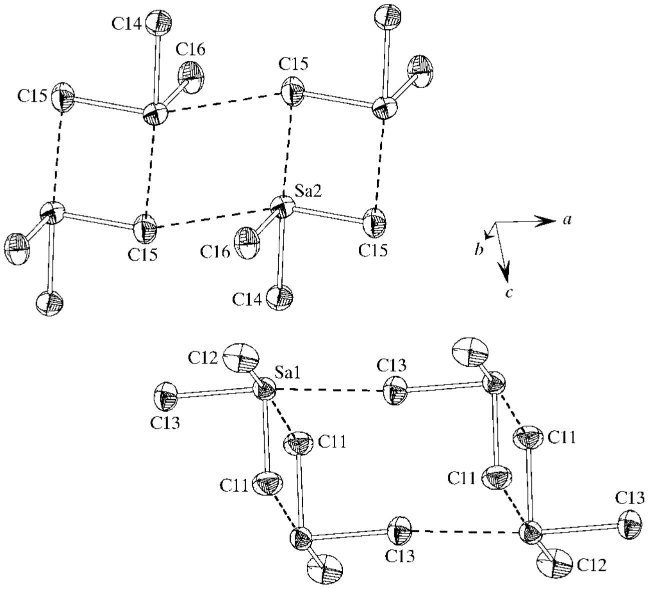


Figure 2
A view of the two types of polymeric species formed by $[SnCl_3]^-$ anions, together with the labelling scheme used in Table 1. Displacement ellipsoids are drawn at the 50% probability level.

DOI: 10.1107/S0108270101020856

divalent metal is well represented by an $SnCl_3$ trigonal pyramid, the two remote Cl atoms contributing only 5% of the Sn^{II} valence (calculated valence: $S = 2.02$ and 1.99 for Sn1 and Sn2, respectively). However, taking the Sn$\cdots$Cl interactions into account, the anions can be considered to form polymeric species, as often described for Sn^{II} compounds, *e.g.* Cs[$SnCl_3$] (Poulsen & Rasmussen, 1970) or [$(C_3H_7)_4N$][SnI_3] (Lode & Krautscheid, 2000), where such (3+2) coordination is also encountered.

In (I), two types of polymeric anion chain are found, both propagating in the [100] direction, one for the $[SnCl_3]^-$ groups containing Sn1 and the other for the $[SnCl_3]^-$ groups containing Sn2 (Fig. 2). The chains are separated by the ammonium groups of the cations which participate in N—H$\cdots$Cl hydrogen bonds (Table 2), thus preventing the formation of polymeric sheets of anions such as those present in Cs[$SnCl_3$].

Experimental

Compound (I) was obtained from a slowly cooled saturated solution containing 2-thienylmethylamine and $SnCl_2 \cdot 2H_2O$ in aqueous HCl. Typically, 2-thienylmethylamine (56 mg, 0.5 mmol) and $SnCl_2 \cdot 2H_2O$ (52 mg, 0.2 mmol) were added under an inert atmosphere to aqueous HCl (4 mol dm^{-3}) at 343 K. After slight evaporation of the solution, slow cooling afforded colourless prismatic crystals of (I).

Crystal data

(C_5H_8NS)[$SnCl_3$]
$M_r = 339.22$
Triclinic, $P\overline{1}$
$a = 5.9937$ (4) Å
$b = 11.9746$ (6) Å
$c = 15.7340$ (10) Å
$\alpha = 75.604$ (5)°
$\beta = 79.802$ (6)°
$\gamma = 86.418$ (5)°
$V = 1076.32$ (11) Å^3

$Z = 4$
$D_x = 2.093$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.1$–15°
$\mu = 3.26$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.4 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.453$, $T_{max} = 0.722$
6286 measured reflections
6282 independent reflections

4790 reflections with $I > 2\sigma(I)$
$R_{int} = 0.074$
$\theta_{max} = 30°$
$h = 0 \rightarrow 8$
$k = -16 \rightarrow 16$
$l = -21 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.118$
$S = 1.12$
6282 reflections
202 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 1.9104P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.24$ e Å^{-3}
$\Delta\rho_{min} = -0.93$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0052 (6)

H atoms were treated as riding, with C—H = 0.93 or 0.97 Å and N—H = 0.89 Å, and with $U_{iso}(H) = 1.5U_{eq}(N)$ or $1.2U_{eq}(C)$.

Table 1
Selected geometric parameters (Å, °).

Sn1—Cl1	2.4951 (13)	Sn2—Cl4	2.5165 (13)
Sn1—Cl2	2.5122 (15)	Sn2—Cl6	2.5257 (14)
Sn1—Cl3	2.5837 (13)	Sn2—Cl5	2.5366 (13)
Sn1—Cl1^{i}	3.4071 (17)	Sn2—Cl5^{iii}	3.5662 (13)
Sn1—Cl3^{ii}	3.4159 (13)	Sn2—Cl5^{iv}	3.5990 (15)
Cl1—Sn1—Cl2	93.16 (5)	Cl4—Sn2—Cl6	90.34 (5)
Cl1—Sn1—Cl3	91.16 (5)	Cl4—Sn2—Cl5	91.23 (5)
Cl2—Sn1—Cl3	90.81 (5)	Cl6—Sn2—Cl5	88.05 (5)
Cl1—Sn1—Cl1^{i}	80.67 (5)	Cl4—Sn2—Cl5^{iii}	76.30 (4)
Cl2—Sn1—Cl1^{i}	173.79 (4)	Cl6—Sn2—Cl5^{iii}	74.16 (4)
Cl3—Sn1—Cl1^{i}	90.03 (4)	Cl5—Sn2—Cl5^{iii}	157.98 (6)
Cl1—Sn1—Cl3^{ii}	83.98 (4)	Cl4—Sn2—Cl5^{iv}	168.17 (4)
Cl2—Sn1—Cl3^{ii}	91.06 (5)	Cl6—Sn2—Cl5^{iv}	79.77 (4)
Cl3—Sn1—Cl3^{ii}	174.88 (6)	Cl5—Sn2—Cl5^{iv}	82.03 (4)
Cl1^{i}—Sn1—Cl3^{ii}	87.60 (4)	Cl5^{iii}—Sn2—Cl5^{iv}	106.79 (3)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$Cl4^{i}	0.89	2.55	3.278 (5)	139
N1—H1$A\cdots$Cl5	0.89	2.83	3.438 (5)	127
N1—H1$B\cdots$Cl3^{i}	0.89	2.46	3.306 (5)	158
N1—H1$C\cdots$Cl4	0.89	2.43	3.303 (5)	168
N2—H2$A\cdots$Cl6^{ii}	0.89	2.43	3.256 (5)	155
N2—H2$B\cdots$Cl3^{ii}	0.89	2.43	3.269 (5)	157
N2—H2$C\cdots$Cl6^{iii}	0.89	2.50	3.386 (6)	177

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

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *MolEN* (Nonius, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *CIFGEN* in *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1180). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Brown, I. D. (1981). *The Bond Valence Method: An Empirical Approach to Chemical Structure and Bonding*, in *Structure and Bonding in Crystals*, Vol. 2, edited by M. O'Keeffe & A. Navtotsky. London: Academic Press.
Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Lode, C. & Krautscheid, H. (2000). *Z. Anorg. Allg. Chem.* **626**, 326–331.
Mercier, N. & Riou, A. (2002). In preparation.
Mitzi, D. B. (1999). *Prog. Inorg. Chem.* **48**, 1–121.
Murray-Rust, P., McManus, J., Lennon, S. P., Porter, A. E. A. & Rechka, J. A. (1984). *J. Chem. Soc. Perkin Trans.* 1, pp. 713–716.
Nonius (1997). *MolEN*. Nonius BV, Delft, The Netherlands.
Poulsen, F. R. & Rasmussen, S. E. (1970). *Acta Chem. Scand.* **24**, 150–156.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.