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$K_3Sn_5Cl_3F_{10}$ with a corrugated layered structure

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(n–Cl) = 0.002 Å
R factor = 0.025
wR factor = 0.058
Data-to-parameter ratio = 13.4

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

Single crystals of $K_3Sn_5Cl_3F_{10}$, tripotassium trichlorodecafluoropentastannate(II), were isolated from a batch of needle-shaped crystals containing several potassium tin(II) fluorides, chlorides and chloride fluorides. The title compound crystallizes in the centrosymmetric space group *Cmcm* and the unit cell contains three crystallographically distinct tin units, with one SnF_3Cl_2E, in the unusual SnX_5E pseudo-octahedral coordination, while the other two are in an SnX_4E pseudo-trigonal bipyramid (E is a stereoactive lone pair). The SnF_3Cl_2 units form $[SnF_2Cl_2]_n^{2n-}$ rows parallel to the a axis of the unit cell, sandwiched between rows of $[Sn_2F_4]_n$ units also parallel to the a axis, with adjacent $[Sn_2F_4]_n$ rows being held together by rows of Cl^- ions, also parallel to a. This ensemble forms $[(Sn_2F_4)(SnF_2Cl_2)(Sn_2F_4)Cl]_n^{3n-}$ anionic planes parallel to ac. Two adjacent anionic planes, their terminal F atoms pointing towards each other, are held together by K^+ ions and form bilayers. Each pair of adjacent bilayers is separated by a sheet of Sn lone pairs, making the structure highly layered.

Comment

Alkali metal and ammonium fluorostannates(II) and chlorostannates(II) have been quite extensively studied and have yielded a variety of unique features, depending on the M/Sn ratio and on the halogen size. The SnF_2/MF systems yield mainly $MSnF_3$ and MSn_2F_5, containing the $[SnF_3]^-$ trifluorostannate(II) and $[MSn_2F_5]^-$ pentafluorostannate(II) ions, respectively.

Divalent Sn-containing halides can exhibit peculiar electrical properties, depending on the other cations present in the solid and the electronegativity of the halogen. For example, in fluorides, divalent Sn has been shown to increase the mobility of the F^- ions in solids by several orders of magnitude, $PbSnF_4$ and $BaSnF_4$ being the best known F^- ion conductors to date. In these compounds, a high energy gap prevents any significant long-range electron mobility. On the other hand, for larger and less electronegative halogens, the energy gap between the valence and conduction bands is much lower, giving rise to semiconducting properties, such as in $CsSnCl_3$ and $CsSnBr_3$, or even metal conductivity, as observed in $CsSnBr_3$ above 418 K (Barrett *et al.*, 1971). Some of these properties have been observed in the compounds obtained by reaction of alkali metal halides MX with stannous fluoride SnF_2 (Kriegsmann & Kessler, 1962). A few recent studies have been carried out on the SnF_2/MCl systems (M are alkali metals and NH_4), prepared both by crystallization from aqueous solutions and by high-temperature reactions in dry conditions. The study of the SnF_2/MCl system (M is Li, Na, K and NH_4) was carried out previously by us (Dénès, 1988; Dénès & Tam, 1988; Dénès *et al.*, 1991).

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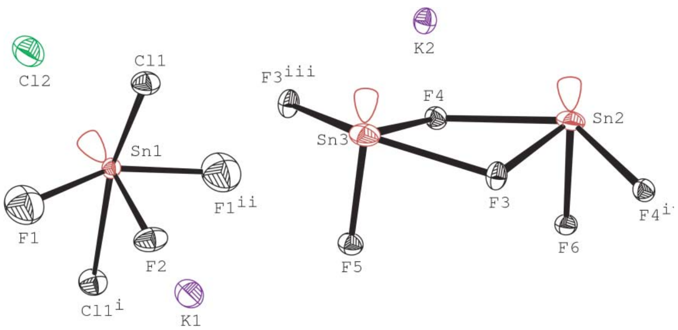

Figure 1
The coordination environment of the metal atoms in (I), with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $-1 + x, y, z$; (iii) $1 + x, y, z$; (iv) $-1 + x, y, z$.]

Crystal structures of a variety of Sn^{II}-containing fluorides, chlorides and chloride fluorides have shown that the Sn^{II} lone pair is located in a hybrid orbital and is therefore highly stereoactive, thereby decreasing the Sn coordination to 3, 4 or 5 and resulting, in most cases, in an SnX_3E pseudo-tetrahedral, SnX_4E pseudo-trigonal biyramidal or SnX_5E pseudo-octahedral coordination, where E, the stereoactive lone pair, occupies a hybrid orbital.

In the present work, single crystals of $K_3Sn_5Cl_3F_{10}$, (I), were isolated and its crystal structure determined. To the best of our knowledge, no structure of a halogenopentastannate(II) has been reported previously.

The unit cell of (I) contains three crystallographically distinct tin units, with one SnF_3Cl_2E (Sn1) in the unusual SnX_5E pseudo-octahedral coordination, while the other two (Sn2 and Sn3) are in an SnX_4E pseudo-trigonal bipyramid (Fig. 1; E is a stereoactive lone pair). The SnF_3Cl_2E pseudo-octahedral units are linked to one another by bridging F^- ions and form $[SnF_2Cl_2]_n^{2n-}$ chains parallel to the a axis of the unit cell. The Sn_2F_4 rings formed by atoms Sn2 and Sn3 are bridged by atoms F3 and F4 to form ribbons parallel to the a axis. Two adjacent layers are held together by Cl^- anions to constitute $[Sn_2F_4Cl]_n^-$ double ribbons (Fig. 2). Between each double ribbon are sandwiched the $[SnF_2Cl_2]_n$ chains, forming $[(Sn_2F_4)(SnF_2Cl_2)(Sn_2F_4)Cl]_n^{3n-}$ anionic planes that are held together by K^+ ions to form neutral bilayers parallel to ac. These corrugated bilayers are separated by sheets of lone pairs from the Sn^{II} atoms, forming effective cleavage planes and making the structure highly two-dimensional (Fig. 3).

Experimental

Thin needle-shaped single crystals of $K_3Sn_5Cl_3F_{10}$ were isolated from a batch of crystals containing several potassium tin(II) fluorides, chlorides and chloride fluorides, such as $KSnCl_3F_2\cdot 4H_2O$, $K_2SnF_6\cdot H_2O$ and Sn_4ClF_7. The crystals were obtained at ambient temperature by slow evaporation of an aqueous solution of potassium chloride and tin(II) fluoride in a $KCl:SnF_2$ ratio of 2:1. Doubly distilled water was used and the solution was gently warmed to make it supersaturated. A Teflon beaker was used and a few drops of 40% HF were added to slow down the hydrolysis of the Sn—F bonds in aqueous solution. A few pellets of tin metal were also added to reduce the slow oxidation of tin(II) to tin(IV).

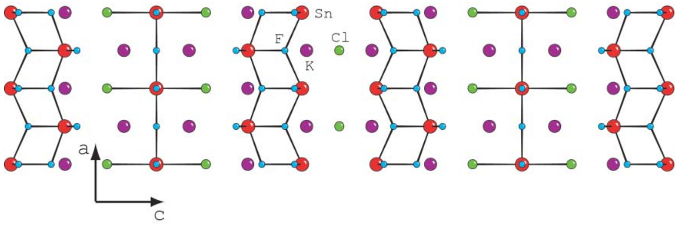

Figure 2
A projection of one layer of the structure of (I) on the ac plane.

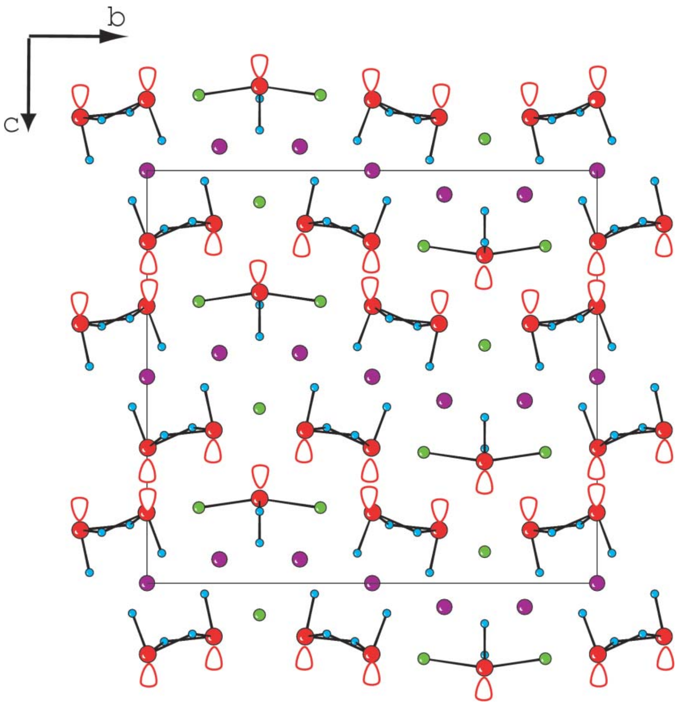

Figure 3
The crystal packing of (I), viewed down the a axis. Lone pairs are shown in idealized positions.

Crystal data

$K_3Sn_5Cl_3F_{10}$
$M_r = 1007.10$
Orthorhombic, $Cmcm$
$a = 4.3051\ (3)$ Å
$b = 19.0324\ (15)$ Å
$c = 20.7335\ (19)$ Å
$V = 1698.8\ (2)$ Å^3
$Z = 4$
$D_x = 3.938$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13477 reflections
$\theta = 2.0$–$29.7°$
$\mu = 8.54$ mm^{-1}
$T = 173\ (2)$ K
Rod, colourless
0.50 × 0.14 × 0.12 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: multi-scan (MULABS in *PLATON*; Spek, 2003)
$T_{min} = 0.106$, $T_{max} = 0.359$
6270 measured reflections
927 independent reflections
919 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 25.5°$
$h = -5 \rightarrow 5$
$k = -22 \rightarrow 22$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.058$
$S = 1.21$
927 reflections
69 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.31$ e Å^{-3}
$\Delta\rho_{min} = -1.07$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sn1—F1	2.230 (3)	Sn2—F4^{i}	2.3565 (15)
Sn1—F2	2.034 (6)	Sn3—F3	2.3693 (15)
Sn1—F1^{i}	2.230 (3)	Sn3—F4	2.293 (4)
Sn1—Cl1^{ii}	2.8297 (17)	Sn3—F5	2.010 (4)
Sn2—F3	2.262 (4)	Sn3—F3^{iii}	2.3693 (15)
Sn2—F4	2.3565 (15)	Sn1—Cl1	2.8297 (17)
Sn2—F6	2.011 (4)		
Cl1—Sn1—Cl1^{ii}	163.18 (6)	F3—Sn3—F4	65.93 (8)
F1—Sn1—F2	74.9 (2)	F3—Sn3—F5	82.28 (10)
F1—Sn1—F1^{i}	149.8 (3)	F3—Sn3—F3^{iii}	130.61 (11)
Cl1—Sn1—F1	87.81 (4)	F4—Sn3—F5	83.79 (14)
Cl1—Sn1—F2	81.59 (4)	F3^{iii}—Sn3—F4	65.93 (8)
F1^{i}—Sn1—F2	74.9 (2)	Sn1—F1—Sn1^{iii}	149.8 (5)
F3—Sn2—F4	66.62 (8)	Sn2—F4—Sn2^{iii}	131.98 (16)
F3—Sn2—F6	86.31 (14)	Sn2—F3—Sn3	111.02 (9)
F4—Sn2—F6	83.37 (10)	Sn2—F4—Sn3	110.39 (9)
F4—Sn2—F4^{i}	131.98 (12)	Sn3—F3—Sn3^{i}	130.61 (16)

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

The highest peak was located at a distance of 1.14 Å from F1 and the deepest hole was located at a distance of 0.52 Å from the same atom.

Data collection: *X-AREA* (Stoe, 2005); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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