Hydrolysis of Tin(II) Fluoride and Crystal Structure of Sn_4OF_6 *

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The hydrolysis of SnF_2 in concentrated aqueous solution resulted in the formation of the tin(II) fluoride oxide, Sn_4OF_6. This is the first evidence for the formation of a basic tin(II) fluoride from an aqueous system. The crystal structure of Sn_4OF_6 has been determined using single-crystal X-ray diffraction and refined by full-matrix least-squares analysis to $R = 0.0199$. The compound crystallises in the orthorhombic space group $P2_12_12_1$ with $a = 16.088(3)$, $b = 10.681(2)$, $c = 4.940(1)$ Å and $Z = 4$. The structure consists of a three-dimensional polymeric network of bridging fluorine and oxygen atoms. Tin is present in four distinct sites one showing tetragonal-based pyramidal geometry while the others all show trigonal-pyramidal geometry with a fourth bridging fluorine atom at 2.4–2.5 Å. The non-bonding electrons are stereochemically active and appear to point into irregular channels which run parallel to the *c* axis.

Tin(II) fluorides have been used extensively in toothpastes and dental preparation as an anti-caries agent. More recently they have become of interest in an entirely different role, as hosts for fluoride-ion conduction for use in fuel-cell applications, *e.g.* KSn_2F_5 [1] and $PbSnF_4$.[2] The continued interest in these materials has meant that the structural chemistry of tin(II) fluorides has been relatively well studied.[3]

There is a considerable amount of evidence to show that Sn^{II} forms very strong bonds to fluorine. The stable and predominant fluorostannate(II) ion in solution is $[SnF_3]^-$ which has a dissociation constant of 1.1×10^{-11} mol dm^{-3} at $I = 2.5$ mol dm^{-3}.[4] In the solid state the $[SnF_3]^-$ tin atom is in a trigonal-pyramidal environment with three short Sn–F bonds and a strongly directional non-bonding lone pair completing a distorted tetrahedral distribution of electron pairs around the element. The Mössbauer parameters for trifluorostannates(II) [5,6] show that the Sn–F bonds contain high tin s character and that the non-bonding electron pair has high tin p character. These observations have been rationalised [7,8] by comparing the relative binding energy of the tin 5s electrons with that for the fluorine 2p electrons. The fluorine 2p electrons have a lower energy than the tin 5s electrons and for this reason any bonding between these elements must involve tin s rather than tin p electrons. A consequence of this is that the tin(II) non-bonding electron pair in the trifluorostannates(II) must have high tin 5p character. In contrast to the situation for tin(II) fluorides the binding energies for chlorine, bromine and iodine np orbitals lie between those for the tin 5s and 5p orbitals and bonds between Sn^{II} and Cl, Br or I will make use of hybridised 5s–5p character. This results in higher tin p character in the Sn–X bonds, weaker Sn–X bonds, lower tin p character in the non-bonding orbital, and less lone-pair distortion.[9]

The extent of hydrolysis of Sn^{II} with increasing pH depends upon the nature of the anions in the aqueous solution. As the pH of a Sn^{II} solution is raised, in the absence of strong complex-forming anions, the basic species $[Sn_3(OH)_4]^{2+}$ precipitates either as its basic salt [*e.g.* $Sn_3(OH)_4(NO_3)_2$ [10]] or as a basic salt of a partially dehydrated species {*e.g.* $[Sn_3O(OH)_2]^{2+}$ in $Sn_3O(OH)_2SO_4$ [11]}. In the presence of strong complexing species such as carboxylate groups or fluoride ions, competition between the complexing anion and hydroxide for bonding to Sn^{II} prevents the formation of $[Sn_3(OH)_4]^{2+}$ and basic salts are not precipitated as the pH is raised. Hydrolysis of Sn^{II} can however, also occur when the temperature of the tin(II) solutions is raised. The product of this hydrolysis reaction is normally hydrous tin(II) oxide [$Sn_3O_2(OH)_2$ [12,13]]. In dilute solutions of SnF_2 hydrolysis does give the hydrous tin(II) oxide but no studies have been carried out on the products of elevated temperature hydrolysis in concentrated solutions. Here we report that on heating concentrated solutions of SnF_2 a white crystalline product previously thought to be an orthorhombic form [14] of SnF_2 is formed. This product is the first crystalline material to be precipitated from the solution before SnF_2 itself crystallises and we now show its true stoichiometry is Sn_4OF_6.

Experimental

An aqueous solution of SnF_2 (1 g, 10 cm^3) was boiled for 10 min, filtered and cooled slowly to give white needles of Sn_4OF_6. These were collected and dried *in vacuo* over KOH pellets (Found: F, 18.7; O, 3.2; Sn, 78.6. Calc. for F_6OSn_4: F, 18.85; O, 2.65; Sn, 78.50%). Tin analysis was carried out by atomic absorption spectroscopy, oxygen by microanalysis and fluorine as dihydrogen hexafluorosilicate (fluorosilicic acid) with titration by thorium nitrate.[15]

Crystallography.—Crystal data. F_6OSn_4, $M = 604.75$, crystal size $0.5 \times 0.1 \times 0.1$ mm, orthorhombic, space group $P2_12_12_1$, $a = 16.088(3)$, $b = 10.681(2)$, $c = 4.940(1)$ Å, $U = 848.9(3)$ Å^3, $T = 291$ K, $D_c = 4.73$ g cm^{-3}, $Z = 4$, white needles, $F(000) = 1048$, μ(Mo-Kα) = 108.61 cm^{-1}.

Data collection and processing. Intensity data were collected on an Enraf–Nonius CAD4 four-circle diffractometer in the ω-2θ scan mode. Monochromatic Mo-Kα ($\lambda = 0.710\,69$ Å) radiation was used throughout. Data for 913 reflections were measured ($1.5 < \theta < 25°$), of which 895 were unique in orthorhombic symmetry and 870 were observed with $I > 3\sigma(I)$

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

and were used in subsequent calculations. Two reference reflections −8 4 0 and 9 2 1 were systematically checked for decay during data collection; no significant decay occurred. Data were corrected for Lorentz and polarisation factors and a semi-empirical absorption correction[16] was applied prior to refinement.

Structure analysis and refinement. Systematic absences in the intensity data lead to an unambiguous space group assignment of $P2_12_12_1$ (no. 19).[17] The structure was solved by direct methods using SHELXS 86[18] and refined using SHELX 76.[19] Scattering factors for neutral atoms were assumed.[20] The tin atoms were located initially, followed by the fluorine atoms which were found by Fourier difference techniques. With all five non-tin atoms located and refined as fluorine and no further atoms evident in the difference map, it was clear that one of those located must in fact be an oxygen atom. Based on the isotropic thermal parameters and bond-length considerations one position seemed the likely oxygen atom. Indeed alternative solutions substituting oxygen onto the other non-tin sites all gave significantly higher R factors. Anisotropic thermal parameters were successfully applied to all atoms. Unitary weights were used in the final refinement, resulting in R = 0.0199 and R' = 0.0243. Refinement in the enantiomorphic configuration resulted in increased R factors. The maximum residual electron density in the final refinement was 0.68 e Å^{-3} with a maximum shift/e.s.d. = 0.105 for the 100 refined parameters. The final atomic parameters are given in Table 1 with contact distances and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Table 1 Final atomic parameters for Sn_4OF_6 with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Sn(1)	0.8413(1)	0.0592(1)	0.1238(2)
Sn(2)	0.9309(1)	0.4490(1)	0.2079(2)
Sn(3)	0.0565(1)	0.2197(1)	0.7143(2)
Sn(4)	0.7336(1)	0.3364(1)	−0.2889(2)
F(1)	0.9551(4)	0.0385(8)	0.3958(16)
F(2)	1.2126(4)	−0.0121(6)	0.1069(15)
F(3)	0.0463(5)	0.0282(6)	−0.0846(15)
F(4)	0.7133(4)	−0.0102(8)	−0.0135(15)
F(5)	1.1294(5)	0.3766(6)	0.4497(16)
F(6)	1.1707(6)	0.2269(7)	−0.0901(15)
O(1)	1.1164(4)	0.1165(7)	0.4249(16)

Table 2 Selected contact distances (Å) and angles (°) in Sn_4OF_6 with e.s.d.s in parentheses

Sn(1)–F(1)	2.282(7)	Sn(3)–F(3)	2.280(7)
Sn(1)–F(4)	2.291(7)	Sn(3)–F(5)	2.428(7)
Sn(1)–F(4a)	2.063(7)	Sn(3)–F(6)	2.077(8)
Sn(1)–F(5c)	2.039(7)	Sn(3)–O(1)	2.047(8)
Sn(2)–F(1c)	2.131(7)	Sn(4)–F(2b)	2.109(7)
Sn(2)–F(2c)	2.518(7)	Sn(4)–F(2c)	2.415(7)
Sn(2)–F(3c)	2.077(7)	Sn(4)–F(6b)	2.234(8)
Sn(2)–O(1c)	2.052(8)	Sn(4)–O(1b)	2.064(7)
F(1)–Sn(1)–F(4)	149.8(3)	F(3)–Sn(3)–F(5)	152.7(3)
F(1)–Sn(1)–F(4a)	78.8(3)	F(3)–Sn(3)–F(6)	83.9(3)
F(1)–Sn(1)–F(5c)	80.0(3)	F(3)–Sn(3)–O(1)	81.7(3)
F(4)–Sn(1)–F(4a)	78.0(1)	F(5)–Sn(3)–F(6)	78.3(3)
F(4)–Sn(1)–F(5c)	81.1(3)	F(5)–Sn(3)–O(1)	76.6(3)
F(4a)–Sn(1)–F(5c)	90.6(3)	F(6)–Sn(3)–O(1)	85.9(3)
F(1c)–Sn(2)–F(2c)	143.4(3)	F(2b)–Sn(4)–F(2c)	74.8(1)
F(1c)–Sn(2)–F(3c)	83.1(3)	F(2b)–Sn(4)–F(6b)	80.8(3)
F(1c)–Sn(2)–O(1c)	81.4(3)	F(2b)–Sn(4)–O(1b)	77.0(3)
F(2c)–Sn(2)–F(3c)	76.7(3)	F(2c)–Sn(4)–F(6b)	155.6(3)
F(2c)–Sn(2)–O(1c)	68.4(3)	F(2c)–Sn(4)–O(1b)	87.3(3)
F(3c)–Sn(2)–O(1c)	89.8(3)	F(6b)–Sn(4)–O(1b)	86.1(3)

Symmetry operations: a $-x + 0.5, -y, 0.5 + z$; b $x + 0.5, -y + 0.5, -z$; c $-x, y + 0.5, -z + 0.5$.

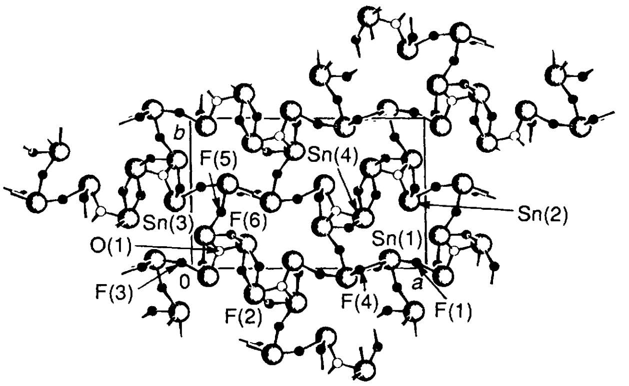

Fig. 1 Projection down the *c* axis of Sn_4OF_6 with the unit cell outlined

Discussion

The fluoride oxide Sn_4OF_6 described in this work is the first reported example of a fluoride oxide of Sn^{II} obtained by hydrolysis in aqueous systems. The only previously reported tin(II) fluoride oxide $Sn_4O_2F_4$[21] was obtained by heating a mixture of solid SnO with solid SnF_2 in a sealed tube at 200 °C.

The crystallisation of Sn_4OF_6 from boiling concentrated aqueous solutions of SnF_2 shows that attack of Sn–F species which are relatively stable at ambient temperatures is possible at elevated temperatures. In very alkaline solutions of Sn^{II} the predominant species is $[Sn(OH)_3]^-$ and solid derivatives of this anion have been isolated.[22] This suggests that Sn–OH bonds are also relatively stable. It seems likely therefore that the first attack on Sn^{II}–F species in boiling solutions involves the replacement of some Sn–F bonds by Sn–O bonds. The final fluoride oxide would then be formed from a cluster containing mainly Sn–F bonds.

The crystal structure of Sn_4OF_6 is built up of a three-dimensional polymeric network of bridging fluorine and oxygen atoms. Four distinct tin sites are present in the structure. The Sn(1) atom has a tetragonal-based pyramidal configuration with four bonding contacts to F 2.04–2.29 Å. The three other tin sites are similarly co-ordinated with two short Sn–F contacts and one short Sn–O contact. A fourth bridging contact to fluorine is also seen in each case but lies outside the sum of the ionic radii at 2.36 Å.[23] Therefore Sn(2), Sn(3) and Sn(4) can be considered to be essentially exhibiting trigonal-pyramidal co-ordination.

All the fluorine atoms bridge two tin atoms unsymmetrically with average contacts of Sn–F 2.20 and Sn ··· F 2.45 Å and F(5) might be considered to bridge three tin atoms with a third contact at 2.51 Å. The O atom has an unusual three-co-ordinate geometry with Sn(2), Sn(3) and Sn(4) almost equidistant at 2.10 Å. The Sn–O–Sn bond angles suggest an almost planar geometry.

The co-ordination geometry of Sn(1) with two short Sn–F bonds and two longer bonds is similar to that seen in other tetragonal-based tin geometries such as $KSnF_3 \cdot \frac{1}{2}H_2O$ (average distances 2.03 and 2.27 Å)[24] and $Na_4Sn_3F_{10}$ (2.04 and 2.26 Å).[25] The Sn(2), Sn(3) and Sn(4) atoms have less typical geometries. The fluoride NH_4SnF_3[26] which contains isolated $[SnF_3]^-$ units in its structure has three equidistant bond lengths of 2.03 Å. A similar bonding scheme to that seen in Sn_4OF_6 has been observed before in $NaSn_2F_5$[27] where two short (average 2.08 Å) and one longer Sn–F bond (2.22 Å) is seen, but the structure of $NaSn_2F_5$ contains essentially isolated $[Sn_2F_5]^-$ units and not a network arrangement.

The stereochemical activity of the non-bonding electron pairs on tin means that close proximity of atoms is not possible in the direction in which the non-bonding electron pairs point. This leads to voids in the structure resulting in irregular channels parallel to the *c* axis. The non-bonding pairs on the tin atoms all point into the channels. The Sn(1) ··· Sn(4) and Sn(2) ··· Sn(3) distances (3.99 and 3.57 Å) are within that normally considered to allow for direct Sn ··· Sn interaction.[28] The compound however showed no evidence for removal of stereochemical activity as seen in $CsSnBr_3$,[29] where the non-bonding electron pairs are fully delocalised into a solid-state conduction band formed by overlap with bromine 4d orbitals. It must therefore be concluded that to a large extent the electron pairs remain localised at the tin site where they exhibit a stereochemically distorting effect.

The polymeric nature of Sn_4OF_6 is not uncommon in tin(II) fluorides. The secondary bridging contacts are similar to those in $Cs_2Sn_6Br_3F_{11}$.[30] The structure is quite unlike that of the parent α-SnF_2,[31,32] which packs in a molecular fashion with discrete Sn_4F_8 puckered rings, but is more closely related to that of β-SnF_2 [33] which also shows a polymeric structure of bridging fluorine atoms. The availability of extra fluorine atoms in the lattice of β-SnF_2 allows the tin atom to adopt essentially four-co-ordinate geometry throughout that structure. The structure of the only other known tin(II) fluoride oxide $Sn_4O_2F_4$ [21] also shows tin in three- and four-co-ordinate geometries. However, this structure has been interpreted in terms of complex anions of $[Sn_2O_2F_4]^{4-}$ held together in the solid state by weak Sn–F interactions leading to a one-dimensional network.

We have previously reported [14] preliminary evidence for an orthorhombic form of SnF_2 based on crystallographic parameters and Mössbauer spectroscopic data. Comparison with the present work suggests that the true stoichiometry is indeed Sn_4OF_6.

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