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SYNTHESIS AND STUDY OF DECAFLUOROHEXATIN(II) HEXAFLUOROTITANATE, $[Sn_6F_{10}][TiF_6]$

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SUMMARY

The compound of composition $TiSn_6F_{16}$ has been synthesized by crystallization from hydrofluoric acid solution. Single crystals were subjected to X-ray structure analysis and the chemical composition of the synthesized compound was determined to be $[Sn_6F_{10}][TiF_6]$. The effect of lone electron pairs (LP) of tin on the crystal structure has been considered.

INTRODUCTION

Tin(II) fluoride compounds are known to exist either as salts (with tin(II) being in anionic or cationic sublattices) or as neutral complexes. Compounds previously studied are M^ISnF_3[1,2,3], $M^{II}(SnF_3)_2$[4,5], $M^ISn_2F_5$[6], $M^{II}(Sn_2F_5)_2$[7] and $M^ISn_3F_{10}$[8]. An example of a neutral complex is $3SnF_2 \cdot SbF_3$[9].

From X-ray data the cationic fluoride particles are polymeric, whereas anionic fluorides particles can exist also as monomers. The only compound with a counterion with a double-negative charge is $[Sn_6F_{10}][Sn^{IV}F_6]$[10] synthesized from aqueous HF solution and which contains $[SnF_6]^{2-}$ and Sn^{2+} ions. The structure of this salt consists of infinite polymeric $(Sn_6F_{10})_n^{2n+}$ layers connected by octahedral SnF_6^{2-} anions.

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The neutral $3SnF_2 \cdot SbF_3$ complex obtained from the aqueous solution [9] contains cyclic Sn_3SbF_9 fragments with four bridging and five terminal fluorine atoms. The structural units are neutral SnF_2 and SbF_3 molecules.

EXPERIMENTAL

The initial chemicals used for the present synthesis were tin difluoride (synthesized by us by dissolution of SnO in 70% hydrofluoric acid, concentration of the solution and precipitation by acetone addition) and titanium dioxide marked "98% pure". After several days of reaction of the concentrated SnF_2 solution in 40% HF in the presence of TiF_6^{2-} anions (in the molar ratio Sn(II):Ti(IV) = 2:1, the $TiSn_6F_{16}$ compound was synthesized (found - 28,1%, F; 66,6%, Sn; calc. - 28,57%, F; 66,93%, Sn). After washing in 3M HF and drying in air, the synthesized colorless transparent crystals had the shape of truncated octahedra. Further studies were performed either on the crystals or on a powder prepared from such crystals.

The IR spectra of the synthesized compound had four absorption bands: 556, 376, 310 and 294 cm^{-1}. The 556 cm^{-1} band is a characteristic of an octahedral TiF_6^{2-} anion [11], three remaining bands are related to Sn-F bonds [12]. Thus the composition of the compound under study was ascribed the formula $[Sn_6F_{10}][TiF_6]$.

An X-ray phase analysis of the $[Sn_6F_{10}][TiF_6]$ powder was performed on a DRON-3.0 diffractometer ($Mo_{K\alpha}$ - radiation, 2θ scanning, scanning angels 4-40°, the scanning rate 1°/min). The X-ray patterns indicated that the specimen consisted of a single phase of unknown composition.

X-ray structure analysis was carried out on a specimen of a spherical shape (R = 0,205 mm). The X-ray experiment was performed on a CAD-4 diffractometer ($Mo_{K\alpha}$ - radiation, $\omega/2\theta$ scanning, $\theta_{max}=40^{\circ}$). The calculations were performed on SM-1700 and IBM PC AT computers by SDP [13] and AE1 [14] programs. The unit cell parameters of the new phase were determined to be monoclinic:a = 18.418(2), b = 7.681(1), c = 10.837(1)Å, β = 90,39(2)°, space group C2/c. Of the total of 5091 recorded reflections, 4108 reflections with $I>3\sigma(I)$ were used for the structure refinement by the least squares procedure with due regard for absorption (μ = 106 cm^{-1}) and secondary-extinction corrections. The refined atomic coordinates are listed in Table 1 (R = 0.027).

TABLE 1

Atomic coordinates of Sn_6TiF_{16}

Atom	x	y	z	$B_{eqv.}$
Sn(1)	0,20802(1)	0,08821(2)	0,18199(1)	1,815(2)
Sn(2)	0,14607(1)	0,38629(2)	0,53231(1)	1,890(2)
Sn(3)	-0,42862(1)	0,32950(2)	0,39697(1)	1,866(2)
Ti	0,000	0,32656(6)	0,250	1,514(6)
F(1)	0,65115(8)	0,3666(2)	0,2557(1)	2,30(2)
F(2)	0,23627(8)	0,3726(2)	0,4060(1)	2,30(2)
F(3)	0,6527(1)	0,1503(2)	0,4587(2)	3,18(3)
F(4)	0,71938(9)	-0,0105(2)	0,6582(1)	2,54(2)
F(5)	0,3691(1)	0,5108(2)	0,4901(2)	3,24(3)
F(6)	0,5668(2)	-0,0076(5)	0,2900(5)	9,4(1)
F(7)	0,4308(2)	0,3328(5)	0,7025(4)	8,8(1)
F(8)	0,5327(3)	0,1646(9)	0,5927(3)	12,0(2)

RESULTS AND DISCUSSION

The synthesized compound melts congruently at 260°C. In the temperature range 300-800°C the compound is oxidized by atmospheric oxygen and at 880°C it rapidly decomposes with the release of gaseous hydrogen fluoride:

$$[Sn_6F_{10}][TiF_6] \xrightarrow{t,air} 6SnO_2 + TiOF_2 + 14HF$$

The $[Sn_6F_{10}][TiF_6]$ structure was determined to be built of $\{[Sn_6F_{10}]^{2+}\}_n$ layers normal to the x-axis (two layers per unit cell) (Fig.1) and TiF_6^{2-} anions occupying special positions on two-fold axes. The Ti-F distances in the TiF_6^{2-} anions range from 1.812(3) to 1.838(4) Å, the valence angles differ from octahedral angles by less than 5°. Interatomic distances and the angles in the coordination polyhedra of tin atoms are given in Table 2. Each tin atom forms a pyramid with three nearest fluorine atoms and the LP presumably occupies the apex, the Sn-F distances being 2.04-2.26 Å and the F-Sn-F angles being 78.0-88.8°. Tin atoms have from three to five additional contacts with other fluorine atoms, the length of such bonds ranging from 2.40 to 3.10 Å.

The Sn(1) atoms have pentagonal-bipyramidal coordination: apical positions are occupied by the $F(5)^b$ and $F(4)^d$ atoms, the equatorial positions are occupied by the $F(1)^a$, $F(2)^b$, $F(3)^c$, $F(7)^e$ atoms and a stereoactive LP between the $F(3)^c$ and $F(7)^e$ atoms. The sum of the angles in the equatorial plane is 361.1°, <u>i.e.</u> the $F(1)^a$, $F(2)^b$, $F(3)^c$ and $F(7)^c$ atoms are sightly displaced from the equatorial plane. The apical fragment is nonlinear - the $F(5)^b$ and $F(4)^d$ atoms are slightly displaced towards the $F(1)^a$ and $F(2)^b$ atoms. This may be an effect of the LP.

If we neglect fluorine atoms laying at distances exceeding 2.55Å from Sn atoms (according to [15], the Sn-F distance for pure ionic interaction is 2.55 Å, for covalent interaction it is 2.12 Å), the coordination polyhedron of the Sn(1) atom is a distorted trigonal bipyramid with the apical positions occupied by the $F(5)^b$ and $F(4)^d$ atoms and equatorial positions occupied by the $F(1)^a$, $F(2)^b$, and a LP (Fig.2).

The coordination polyhedron of the Sn(2) atom is a three capped trigonal prism. The triangular bases are formed by the $F(3)^g$, $F(6)^g$, $F(8)^g$ and $F(1)^f$, $F(2)^e$, $F(5)^e$ atoms, respectively, and are almost parallel to one another; the side faces are centered with F(2), $F(4)^g$ atoms and a stereoactive LP. The nearest environment of Sn(2) atom consists of three fluorine atoms, and therefore it's coordination polyhedron is transformed into a trigonal pyramid with the LP at the apex and the F(2), $F(3)^g$ and $F(4)^g$ atoms in the base (Fig.3). Such a coordination polyhedron is very typical for tin fluorides with an anionic sublattice built by tin-fluoride species.

TABLE 2

Bond lengths (d,Å) and angles (ω,°) in coordination environments of tin(II)

Atoms	d	Atoms	ω	Atoms	ω	Atoms	ω
Sn(1)F(1)^{a}	2,155(1)	F(1)^{a}Sn(1)F(2)^{b}	78,00(5)	F(3)^{g}Sn(2)F(4)^{g}	81,15(6)	F(1)^{h}Sn(3)F(3)^{h}	80,01(6)
Sn(1)F(2)^{b}	2,172(1)	F(1)^{a}Sn(1)F(5)^{b}	78,81(6)	F(3)^{g}Sn(2)F(8)^{g}	58,0(1)	F(1)^{h}Sn(3)F(7)^{i}	67,19(9)
Sn(1)F(3)^{c}	3,029(2)	F(2)^{b}Sn(1)F(4)^{d}	81,69(5)	F(4)^{g}Sn(2)F(8)^{g}	91,97(9)	F(3)^{h}Sn(3)F(6)^{h}	63,80(9)
Sn(1)F(4)^{d}	2,258(1)	F(3)^{c}Sn(1)F(4)^{d}	85,89(5)	F(5)^{e}Sn(2)F(8)^{g}	130,4(1)	F(5)^{i}Sn(3)F(6)^{h}	143,67(9)
Sn(1)F(5)^{b}	2,408(2)	F(4)^{d}Sn(1)F(5)^{b}	150,38(6)	F(1)^{f}Sn(2)F(2)^{e}	52,87(4)	F(6)^{h}Sn(3)F(7)^{i}	133,3(1)
Sn(1)F(7)^{e}	2,917(4)	F(1)^{a}Sn(1)F(3)^{c}	136,53(5)	F(1)^{f}Sn(2)F(5)^{e}	56,09(4)	F(1)^{h}Sn(3)F(5)^{i}	88,83(6)
		F(1)^{a}Sn(1)F(7)^{e}	64,91(8)	F(2) Sn(2)F(2)^{e}	63,47(4)	F(1)^{h}Sn(3)F(8)^{h}	147,8(1)
Sn(2)F(1)^{f}	3,101(1)	F(2)^{b}Sn(1)F(5)^{b}	75,53(6)	F(2) Sn(2)F(5)^{e}	88,35(5)	F(3)^{h}Sn(3)F(7)^{i}	136,3(1)
Sn(2)F(2)	2,162(1)	F(3)^{c}Sn(1)F(5)^{b}	98,40(6)	F(2)^{e}Sn(2)F(3)^{g}	130,69(5)	F(5)^{i}Sn(3)F(7)^{i}	71,40(9)
Sn(2)F(2)^{e}	3,012(1)	F(4)^{d}Sn(1)F(7)^{e}	104,01(8)	F(2)^{e}Sn(2)F(6)^{g}	133,97(8)	F(6)^{h}Sn(3)F(8)^{h}	83,0(2)
Sn(2)F(3)^{g}	2,182(2)	F(1)^{a}Sn(1)F(4)^{d}	78,12(5)	F(3)^{g}Sn(2)F(5)^{e}	154,01(6)	F(1)^{h}Sn(3)F(6)^{h}	81,30(9)
Sn(2)F(4)^{g}	2,068(1)	F(2)^{b}Sn(1)F(3)^{c}	59,69(5)	F(4)^{e}Sn(2)F(5)^{e}	119,40(5)	F(3)^{h}Sn(3)F(5)^{i}	80,11(7)
Sn(2)F(5)^{e}	3,072(2)	F(2)^{b}Sn(1)F(7)^{e}	139,87(8)	F(5)^{g}Sn(2)F(6)^{g}	98,76(8)	F(3)^{h}Sn(3)F(8)^{h}	67,9(1)
Sn(2)F(6)^{g}	3,100(5)	F(3)^{c}Sn(1)F(7)^{e}	158,45(8)	F(6)^{f}Sn(2)F(8)^{g}	71,31(9)	F(5)^{i}Sn(3)F(8)^{h}	87,4(1)
Sn(2)F(8)^{g}	3,061(6)	F(5)^{b}Sn(1)F(7)^{e}	82,59(9)	F(1)^{f}Sn(2)F(3)^{g}	149,86(5)	F(7)^{i}Sn(3)F(8)^{h}	140,1(2)
				F(1) Sn(2)F(6)^{g}	146,61(7)		
Sn(3)F(1)^{h}	2,147(1)	F(1)^{f}Sn(2)F(2)	116,33(5)	F(2) Sn(2)F(3)^{g}	76,63(6)		
Sn(3)F(3)^{h}	2,137(2)	F(1)^{f}Sn(2)F(4)^{g}	73,21(5)	F(2)^{e}Sn(2)F(6)^{g}	80,61(8)		
Sn(3)F(5)^{i}	2,044(2)	F(1)^{f}Sn(2)F(8)^{g}	106,71(8)	F(2)^{e}Sn(2)F(4)^{g}	69,04(5)		
Sn(3)F(6)^{h}	2,837(4)	F(2) Sn(2)F(4)^{g}	86,25(6)	F(2)^{g}Sn(2)F(8)^{g}	154,69(6)		
Sn(3)F(7)^{i}	2,808(4)	F(2) Sn(2)F(8)^{g}	134,2(1)	F(3)^{g}Sn(2)F(6)^{g}	58,29(8)		
Sn(3)F(8)^{h}	2,537(4)	F(2)^{e}Sn(2)F(5)^{e}	55,02(4)	F(4) Sn(2)F(6)^{g}	139,20(8)		

The coordinates of letter-marked atoms were calculated by:a- x-1/2,y-1/2,z;b- 1/2-x,y-1/2,1/2-z; c- 1-x,y,1/2-z;d- 1-x,$\bar{y}$,1-z;e- 1/2-x,1/2-y,1-z;f- x-1/2,1/2-y,1/2+z;g- x-1/2,y+1/2,z;h- x-1,y,z; i- $\bar{x}$,1-y,1-z

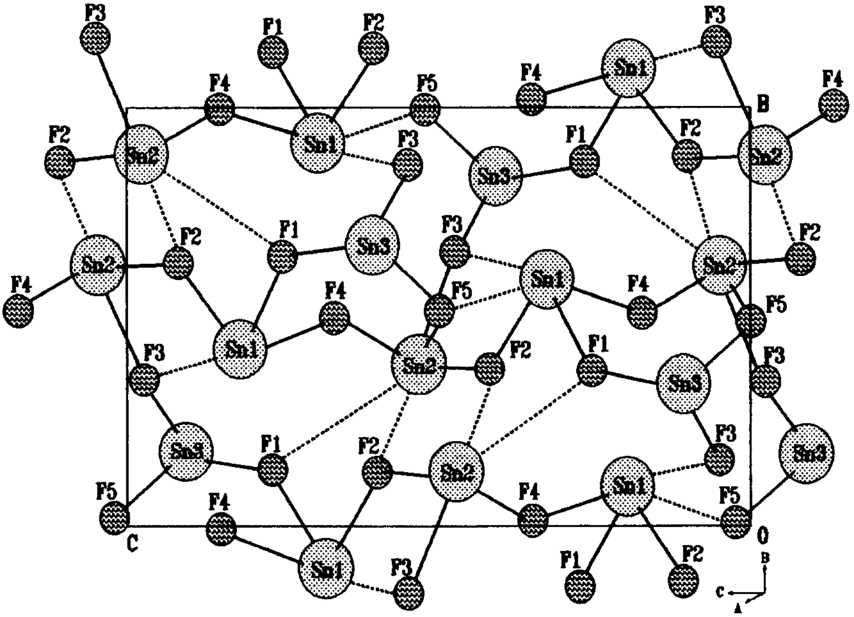

Fig. 1. The layer of $\{[Sn_6F_{10}]^{2+}\}_n$ in projection on the yz plane.

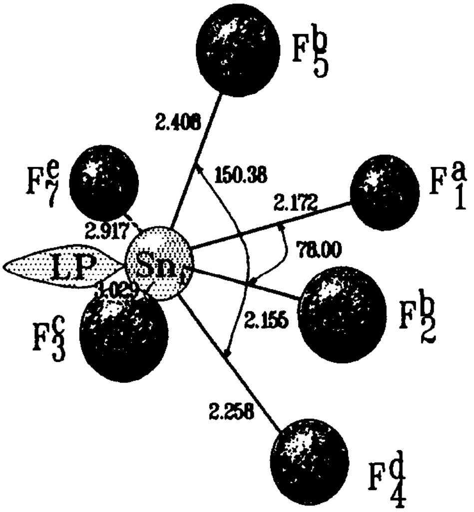

Fig. 2. The coordination environment of Sn(1) in the $[Sn_6F_{10}][TiF_6$

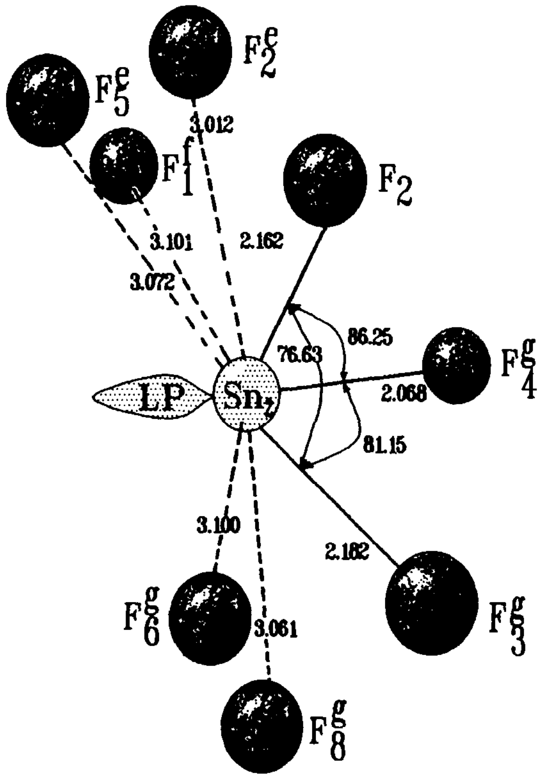

Fig. 3. The coordination environment of Sn(2) in the $[Sn_6F_{10}][TiF_6]$.

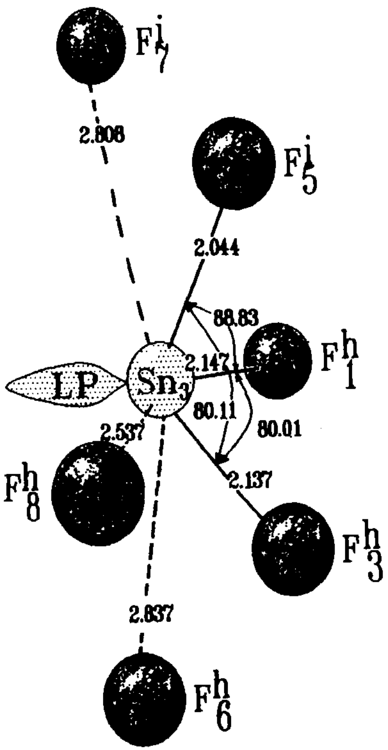

Fig. 4. The coordination environment of Sn(3) in the $[Sn_6F_{10}][TiF_6]$.

The coordination polyhedron of Sn(3) atoms is close to one-capped octahedron whose $F(6)^h$-$F(7)^i$-$F(8)^h$ face is centered with a LP. The atoms forming this face are located at a distance of 2.57-2.84 Å from the Sn(3) atom whereas the atoms forming the opposite face are located at a distance of 2.04-2.15 Å from Sn(3). The Sn(3) atom lies almost in the plane of the centered face (displaced from it by 0.28 Å).

Considering the environment of the Sn(3) atom allowing for the fact that the maximum distance between F and Sn atoms is 2.57 Å, we see that the coordination polyhedron of Sn(3) is a distorted trigonal bipyramid with the $F(1)^h$ and $F(8)^h$ atoms at apexes and F(3) and $F(5)^i$ atoms and the LP in equatorial positions. With the maximum Sn-F distance 2.55 Å, the coordination polyhedron consists of three fluorine atoms and a LP (Fig.4).

In structure $3SnF_2\cdot SbF_3$ [9] there are two kinds of crystallographically nonequivalent SnF_2 molecules forming infinite spiral ribbons along the [010] axis. Allowing for bridge-like bonds, the coordination polyhedron of Sn(1) atoms is a distorted trigonal bipyramid with a LP in the equatorial plane and that of Sn(2) atom is a trigonal pyramid with a LP at the apex. The $2SnF_2\cdot SbF_3$ sublimed from the melt is built up from $[Sn_3F_4]^{2+}$ and $[SnF_4]^{2-}$ ions separated by SbF_3 molecules [16]. The $(Sn_3F_3)^{3+}[AsF_6]^-_3$ compound was synthesized by reaction between tin(II) fluoride and arsenic pentafluoride [17]. It consists of cyclic trimeric cation fragments with three bridge fluorine atoms. All tin atoms in the structure are crystallographically equivalent. The coordination polyhedron can be described as a distorted trigonal SnF_4LP bipyramid with two bridge F atoms from the $Sn_3F_3^{3+}$ cycle and a LP located in the equatorial plane. The apical positions are occupied by the fluorine atoms of AsF_6^- octahedra. The typical feature of $[Sn_2F_3][BF_4]$ [18] is polymer $[Sn_2F_3]^{n+}_n$ chains with incorporated tetrahedral BF_4^- anions. The $[Sn_3F_5][BF_4]$ [18] structure is built by layers of bound $Sn_6F_{10}^{2+}$ rings separated by layers of BF_4^- anions. Some mixed halogenofluorides can also be related to cationic tin(II) complexes. Orthorhombic Sn_2ClF_3 and monoclinic Sn_3BrF_5 [19] consist of infinite three-dimensional cationic $(Sn_2F_3)^{n+}_n$ and $(Sn_3F_5)^{n+}_n$ frameworks with voids occupied by

TABLE 3

Structural data of some tin(II) fluorocomplexes

Compound	1	2	3	4	5	6	7	8	9
References	our data	[4]	[5]	[10]	[11]	[13]	[13]	[1]	[12]
SnF_3E									
Distances Sn-F, Å	2.162 2.182 2.068	2.053 2.096 2.081	2.035 2.048 2.056			2.15 2.21 2.12 2.15 1.99 2.21	2.18 2.11 2.20 2.11 2.19 2.10		2.09 ± 2
Angles F-Sn-F, °	76.63 81.15 86.25	82.6 82.0 87.3	84.2 84.5 86.1			88.4 79.4 75.0 80.2 82.2 78.6	78.8 80.9 80.0 81.9 78.5 81.4		84 ± 4
SnF_4E									
Distances Sn-F, Å	2.408 2.573 2.155 2.044 2.172 2.137 2.268 2.147	-	-	2.478 2.075 2.063 2.218	2.587 2.587 2.097 2.097			2.27 2.27 2.04 2.04	-
Angles F-Sn-F, °	78.84 87.4 75.53 67.9 78.00 80.11 81.69 80.01 78.12 88.83 150.38 147.8	-	-	84.4 82.9 82.9 82.1 82.8 158.6	74.2 74.2 83.0 74.2 74.2 136.0			89.7	-

1.-$[Sn_6F_{10}][TiF_6]$, $[N_2H_6](SnF_3)_2$-2, $Cd(H_2O)_6(SnF_3)_2$-3, $3SnF_2 \cdot SbF_3$-4, $(Sn_3F_3)(AsF_6)_3$-5, Sn_3BrF_5-6, Sn_2ClF_3-7, $KSnF_3 \cdot 1/2H_2O$-8, $(Sn_2F_3)(BF_4)$-9 halogen anions. The Sn-Hal distances (Hal = Cl, Br) exceed the sums of Van-der-Waals radii.

Table 3 lists the Sn-F bond lengths and F-Sn-F valence angles for some cationic and anionic fluoride complexes of tin(II). The mean Sn-F distance in cation complexes of SnF_3LP (e.g. in $[Sn_6F_{10}][TiF_6]$) is 2.13 Å, the same distance in anion complexes (e.g. in $Cd(H_2O)_6(SnF_3)_2$) is 2.04 Å. The mean values of the F-Sn-F angles are 81.3 and 84.9°, respectively. Analysis of respective distances and angles in other complexes shows that the mean Sn-F distance in anionic complexes (~2.05 Å) is smaller than in cationic ones (~2.15 Å). On the contrary, the F-Sn-F angles for anions (84.3°) are larger than those for cations (80.6°). If in accordance with Gillespie and Nyholm model, the steric activity of LP manifests itself in a decrease of the angle between the ligands and in an increase of the tin(II)-ligand distance, one can assume that the steric chemical activity of a LP of the SnF_3LP environment in anions is lower than in cations. This can be explained by additional shielding of a LP by extra electrons in anions.

The mean Sn-F distance in the SnF_4LP group in the $KSnF_3 \cdot 1/2H_2O$ structure is 2.16 Å, i.e., it almost coincides with the corresponding distance for neutral $3SnF_2 \cdot SbF_3$ complex. But for the cation fluorides its mean value is 2.27 Å. The mean value of F-Sn-F angles in cations is much smaller than in anions (78.4° and 89.7°, respectively), and even for a neutral complexe it is 83.0°. Thus, in the case of a distorted trigonal-bipyramidal coordination polyhedron of the Sn(II) atom, the steric chemical activity of anions is lower than that of cations.

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