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The Crystal Structure of Sodium Pentafluorodistannate(II), $NaSn_2F_5$*

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The crystal structure of sodium pentafluorodistannate(II), $NaSn_2F_5$, has been determined from single-crystal X-ray data. The compound is tetragonal, space group $P4_2/nbc$, with $a = 9{\cdot}020$ and $c = 13{\cdot}685$ Å, and there are eight formula units per unit cell. Anisotropic least-squares refinement was made with a final R of 5·6%. Discrete $Sn_2F_5^-$ groups are observed. These complex ions consist of two SnF_2 groups bridged by a fluorine atom lying on a twofold axis. The $Sn_2F_5^-$ groups are linked by two Sn–F bonds of 2·53 Å so that infinite chains of these groups lie parallel to **c**. The Sn–F distance in the bridge is 2·22 ± 0·01 Å and the other Sn–F distances are 2·07 ± 0·02 and 2·08 ± 0·02 Å. Sodium atoms have both six and eightfold coordination with fluorine atoms.

Introduction

The sodium pentafluorodistannate(II), $NaSn_2F_5$, used in this investigation was obtained from Dr W. Nebergall of the Chemistry Department, Indiana University. It had been prepared by mixing equal quantities of 1-molar solutions of NaF and SnF_2 in contact with a small amount of metallic tin to assure a +2 oxidation state for the tin. Crystals were formed by evaporating the solution. We were originally informed that the crystals were $NaSnF_3$ but the structure determination has proven that the compound is actually $NaSn_2F_5$.

This compound is of interest because of its use in research on the inhibition of dental caries by fluoride ions. Some of the properties of this material in solution have been reported by Schaap, Davis & Nebergall (1954).

Experimental

The refractive indices of $NaSn_2F_5$ are $\omega = 1{\cdot}650 \pm 0{\cdot}004$ and $\varepsilon = 1{\cdot}700 \pm 0{\cdot}004$. Preliminary Weissenberg and precession photographs showed the unit cell to be tetragonal and the systematic extinctions uniquely establish the space group to be $P4_2/nbc$. Lattice constants were measured with a carefully aligned single-crystal orienter on an XRD 5 X-ray diffraction unit and found to be $a = 9{\cdot}020 \pm 0{\cdot}003$ and $c = 13{\cdot}685 \pm 0{\cdot}003$ Å (λ Mo $K\alpha = 0{\cdot}70926$ Å). The measured density was 4·2 g.cm^{-3} and the calculated density with 8 $NaSn_2F_5$ formula units per unit cell is 4·24 g.cm^{-3}.

The crystals are long tetragonal prisms bounded by {110} and {001}. Such a crystal with approximate dimensions $21 \times 21 \times 184\ \mu$ was mounted on the c axis and intensities were measured with the single-crystal orienter. Mo $K\alpha$ radiation and the balanced filter technique were used. Only the asymmetric portion of the sphere was investigated. Within the range $2\theta \le 50°$, 210 out of a possible 497 reflections were observed. The size and shape of the crystal were such that absorption corrections were trivial and none were applied.

Determination of the structure

The compound was originally thought to be $NaSnF_3$ with 16 formula units per unit cell; no precise density measurement had been made although the density was known to be greater than 4·0 g.cm^{-3}. A three-dimensional sharpened Patterson function was initially computed and a tin atom in the sixteenfold general set was located at $x \simeq 0{\cdot}577$, $y \simeq 0{\cdot}423$ and $z \simeq 0{\cdot}125$. (The origin has been placed at a center of symmetry.) Ordinarily a heavy-atom structure, such as this one, would be easily determined by a process of Fourier refinement once the location of the heavy atom was known. In the present case the heavy atom is in a rather 'special' general position; *i.e.* $x, \bar{x}, \frac{1}{8}$. These particular values cause the tin atom to contribute very little to a great many of the reflections and therefore the signs of most of the weak reflections are not fixed by the heavy atom. A Fourier synthesis computed with only the limited class of reflections whose signs were fixed by the tin atom had false symmetry and spurious peaks, and it was not possible to interpret the results.

A difference Patterson function, with the Sn–Sn vectors removed, was next computed. From this Patterson function it was deduced that light atoms occupied the fourfold sets (a) and (c) and also the general set with $x \simeq 0{\cdot}347$, $y \simeq y_{\mathrm{Sn}}$ and $z \simeq z_{\mathrm{Sn}}$. No attempt was made at this point to distinguish between the isoelectronic Na^+ and F^- ions. Their identities were later established on the bases of interatomic distances and stoichiometry. A difference Fourier was

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then computed with the tin atom and the three above mentioned light atoms removed. Many obviously spurious peaks again resulted but there were peaks in plausible positions.

A rather frustrating situation then arose. When a particular position was chosen for an additional light atom, and a series of least-squares calculations followed by a difference Fourier synthesis was made, the difference Fourier synthesis showed a negative region at the assumed light atom position (indicating that the atom was really not there) and a positive peak at some unrelated position (indicating that this was really the position of the light atom). When the additional atom was placed in the position suggested by the positive peak, and the least-squares and difference Fourier calculations repeated, the positive and negative peaks interchanged their positions. Furthermore, the assumed unit cell contents of 16 $NaSnF_3$ were never realized. In all of the above calculations, the Sn atom was initially placed at $z=0\cdot125$ and it always moved to $z\simeq0\cdot130$.

We then suspected that the assumed formula, $NaSnF_3$, was incorrect. A density measurement was made and the density was found to be 4·2 $g.cm^{-3}$. The only formula compatible with this density is $NaF.2SnF_2$ or $NaSn_2F_5$, with eight formula units per unit cell. A flame photometer sodium analysis was later performed and gave 7·1% Na, much closer to the 6·5% calculated for $NaSn_2F_5$ than the 11·5% calculated for $NaSnF_3$.

With this new information, and the information from the Patterson functions and difference Fourier syntheses that had been computed, a structure was postulated with sodium in the fourfold sets (*a*) and (*c*), fluorine in two sixteenfold general sets and one eightfold set (*j*), and tin in the general set. All atoms were near what proved to be their final positions. Least-squares refinement reduced *R* to 12%, a value about twice what we had expected. Then, a least-squares refinement was started with the initial value of $z_{\rm Sn}=0\cdot124$ rather than 0·125. This time, $z_{\rm Sn}$ was decreased to 0·119, rather than increasing to 0·130, all atoms quickly converged, and *R* was reduced to 6·6%.

Finally, an anisotropic least-squares refinement was made, giving a final *R* of 5·6%. The final changes, expressed as fractions of their standard deviations, were $<6\times10^{-5}$ for all parameters. The quantity minimized was $\Sigma(\Delta F)^2$. Form factors were used in exponential form with parameters given by Forsyth & Wells (1959). The final least-squares parameters are given in Tables 1 and 2 and the structure factors calculated with these parameters, along with the observed structure factors, are given in Table 3.

Table 1. *Final least-squares position parameters for* $NaSn_2F_5$

Origin is at $\bar{1}$

Atom	*x*	*y*	*z*
Sn	0·5698 ± 0·0003	0·4155 ± 0·0003	0·1192 ± 0·0002
F(1)	0·4596 ± 0·0027	0·3815 ± 0·0026	−0·0496 ± 0·0013
F(2)	0·3431 ± 0·0024	0·4007 ± 0·0026	0·1382 ± 0·0013
F(3)	0·5600 ± 0·0029	0·5600 ± 0·0029	$\frac{1}{4}$
Na(1)	$\frac{1}{4}$	$\frac{1}{4}$	0
Na(2)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$

The standard deviation of the electron density was estimated by Cruickshank's (1949) method to be 0·5 e.Å^{-3}. A final difference Fourier synthesis was computed with all anisotropic atoms removed. There are positive regions as high as 1·5 and negative regions as low as −1·9 e.Å^{-3}. The largest peaks are in the vicinity of the tin atom and are typical of difference Fourier peaks in which the anisotropic thermal parameters have not been properly accounted for. The probable reason for this feature is that there are many weak reflections, particularly those with *l* odd, which are of relatively low accuracy, and the least-squares procedure is adjusting the thermal parameters to account for these experimental discrepancies. Consequently the thermal parameters probably have only qualitative significance.

Because the difference Fourier synthesis raised some doubt about the correctness of the results, *R* was calculated for various classes of reflections to see if any systematic variations occurred. The results are given in Table 4. For classes with *l* odd, *R* is about 10%. For all other classes, *R* is about 6%. We believe this difference is a consequence of the lower accuracy with which the weaker reflections were measured rather than of an error in the structure determination.

Discussion of the structure

In Table 5 the various interatomic distances and angles are given. All standard deviations were computed from the inverse matrix and correlation terms have been included. The anisotropic thermal parameters were transformed to obtain the ellipsoids of

Table 2. *Final least-squares thermal parameters for* $NaSn_2F_5$

Atom	$B_{11}\times10^5$	$B_{22}\times10^5$	$B_{33}\times10^5$	$B_{12}\times10^5$	$B_{13}\times10^5$	$B_{23}\times10^5$
Sn	476 ± 38	425 ± 38	290 ± 11	−53 ± 49	−49 ± 56	−59 ± 55
F(1)	881 ± 386	787 ± 332	191 ± 113	767 ± 580	390 ± 353	528 ± 327
F(2)	892 ± 319	732 ± 359	60 ± 92	242 ± 529	157 ± 317	−88 ± 344
F(3)	1064 ± 352	$B_{22}=B_{11}$	160 ± 133	444 ± 1129	203 ± 427	$B_{23}=B_{13}$
Na(1)	10 ± 431	1059 ± 670	306 ± 132			
Na(2)	876 ± 473	$B_{22}=B_{11}$	29 ± 106	585 ± 1234		

Table 3. *Observed and calculated structure factors for* $NaSn_2F_5$

The column headings are l, F_o and F_c. If $F_o < 0$, the minus sign means 'less than'

H= 0 K= 0		
2	75	74
4	569	-602
6	155	-151
8	516	519
10	-58	1
12	275	-268
14	97	-110
16	191	195
H= 0 K= 2		
0	409	429
1	56	-56
2	-32	33
3	-34	-27
4	335	-346
5	-32	23
6	112	-101
7	-35	24
8	182	182
9	-30	0
10	40	36
11	-25	9
12	173	-175
13	-42	28
14	72	-75
15	-40	4
H= 0 K= 4		
0	223	-227
1	131	-138
2	29	-20
3	-25	24
4	281	279
5	58	63
6	35	14
7	-37	-24
8	107	-106
9	-40	-20
10	-39	-9
11	-44	50
12	121	127
13	-47	51
14	-45	7
15	-41	-14
H= 0 K= 6		
0	459	-462
1	56	-55
2	37	-22
3	49	51
4	320	310
5	39	35
6	78	86
7	42	-48
8	324	-312
9	-36	-14
10	59	-78
11	47	40
12	146	160
13	-46	18
H= 0 K= 8		
0	195	-199
1	75	73
2	-35	4
3	-35	-46
4	210	219
5	69	-62
6	-49	59
7	-38	23
8	149	-155
9	-45	28
10	64	-56
H= 0 K= 10		
0	-45	10
1	94	105
2	-40	2
3	76	-72
4	-50	-52
5	65	-79
H= 1 K= 1		
0	-26	-17
2	-28	13
4	165	-164
6	-32	-31
8	-35	19
10	52	66
12	93	-73
14	-45	-32
16	-43	5
H= 1 K= 2		
1	-32	-28
2	441	-456
3	40	-43
4	-31	-38
5	165	165
6	382	376
7	-36	49
8	116	105
9	-35	-23
10	229	-228
11	-42	-35
12	106	-95
13	47	24
14	117	130
15	-47	-23
H= 1 K= 3		
0	254	257
1	-32	-25
2	-29	19
3	43	46
4	181	-177
5	31	22
6	43	-45
7	54	-39
8	213	202
9	39	-19
10	72	88
11	-26	14
12	79	-70
13	-43	3
14	64	-61
15	-41	-12
H= 1 K= 4		
1	66	67
2	482	-485
3	-33	7
4	57	-65
5	44	38
6	377	356
7	37	-19
8	68	70
9	41	41
10	252	-242
11	-36	-8
12	71	-67
13	-44	-1
14	150	155
15	-32	-24
H= 1 K= 5		
0	97	92
1	-31	-21
2	-31	3
3	61	63
4	216	-203
5	37	42
6	-35	-7
7	-42	-45
8	79	75
9	56	-42
10	45	39
11	-37	14
12	83	-89
13	-30	15
14	-41	-12
H= 1 K= 6		
1	98	93
2	108	-102
3	49	57
4	50	-48
5	-40	-56
6	-43	33
7	73	-78
8	-35	0
9	58	55
10	-42	-44
11	-38	39
12	-30	-8
13	-46	-17
H= 1 K= 7		
0	-37	-7
1	-37	-11
2	-37	-6
3	-44	18
4	-44	52
5	-34	24
6	-40	17
7	-27	-15
8	-37	4
9	-38	-41
10	-29	-8
11	-45	-11
12	51	33
H= 1 K= 8		
1	67	59
2	191	192
3	-47	62
4	-36	7
5	-37	-37
6	179	-179
7	61	-56
8	48	-42
9	-39	29
10	105	116
H= 1 K= 9		
0	123	-136
1	-37	7
2	-43	-19
3	-29	6
4	73	81
5	-29	9
6	-45	21
7	-45	7
8	87	-89
H= 1 K= 10		
1	-30	-1
2	178	189
3	-30	13
4	-40	32
5	-31	7
H= 2 K= 2		
0	293	299
2	-30	-2
4	89	-77
6	63	-57
8	176	173
10	-33	22
12	-48	-39
14	50	-54
H= 2 K= 3		
1	-33	12
2	-30	0
3	-28	-24
4	-33	-24
5	-33	19
6	61	-56
7	-37	36
8	50	-38
9	-40	22
10	43	19
11	-44	-38
12	-37	31
13	-44	-6
14	-31	0
15	-47	21
H= 2 K= 4		
0	200	-188
1	70	-67
2	-34	-35
3	-26	4
4	52	43
5	-38	38
6	-34	25
7	-38	0
8	101	-90
9	-34	-14
10	-27	-6
11	-42	21
12	-43	32
13	-45	37
14	-47	27
H= 2 K= 5		
1	-32	-21
2	256	-248
3	-33	-15
4	71	-64
5	-23	-5
6	185	182
7	-33	29
8	64	60
9	-35	-3
10	141	-143
11	-43	-16
12	63	-72
13	-41	-2
14	92	96
H= 2 K= 6		
0	185	-180
1	49	-44
2	-35	-10
3	-39	18
4	209	209
5	-40	26
6	-44	52
7	-39	-22
8	123	-123
9	-37	-25
10	-47	-49
11	-30	15
12	113	113
13	52	24
H= 2 K= 7		
1	-38	12
2	232	-241
3	-42	34
4	-43	-35
5	-40	-20
6	229	217
7	-42	-16
8	71	70
9	-39	4
10	148	-157
11	-46	27
H= 2 K= 8		
0	143	-141
1	-41	30
2	-41	6
3	-36	-3
4	70	83
5	-37	-13
6	-38	25
7	-29	7
8	117	-119
9	-31	10
10	-41	-32
H= 2 K= 9		
1	-50	54
2	82	-81
3	-51	70
4	-30	5
5	-49	-57
6	86	84
7	-50	-56
8	-31	13
H= 2 K= 10		
0	-40	34
1	-40	43
2	-31	13
3	-41	-39
4	-31	-4
H= 3 K= 3		
0	389	388
2	-33	38
4	551	-543
6	63	-65
8	306	295
10	150	152
12	239	-240
14	80	-83
H= 3 K= 4		
1	-31	-24
2	-34	-6
3	61	-58
4	-33	5
5	-34	21
6	-38	37
7	-37	22
8	-38	30
9	-35	-4
10	-41	-14
11	-38	-26
12	-44	-28
13	-31	17
14	-32	4
H= 3 K= 5		
0	329	315
1	-37	-45
2	-34	33
3	84	85
4	274	-256
5	61	59
6	-33	-26
7	64	-70
8	229	220
9	69	-65
10	60	65
11	-44	21
12	119	-117
13	-47	22
H= 3 K= 6		
1	-39	-11
2	-24	-10
3	-43	-36
4	41	0
5	-34	-5
6	-39	6
7	-36	-22
8	-37	-6
9	-38	-9
10	-39	-4
11	-31	3
12	-47	2
H= 3 K= 7		
0	132	-125
1	42	-43
2	-34	-5
3	-46	73
4	-40	47
5	68	74
6	-37	18
7	-43	-44
8	83	-85
9	75	-75
10	-41	-10
11	-42	11
H= 3 K= 8		
1	-42	16
2	-28	16
3	-37	14
4	-29	10
5	-38	-22
6	-30	-12
7	-40	-31
8	-46	-15
9	-47	2
H= 3 K= 9		
0	204	-219
1	-39	-24
2	-39	-24
3	-30	16
4	220	227
5	-40	23
6	-47	46
7	-42	-11
H= 3 K= 10		
1	-47	20
2	-47	27
3	-42	23
H= 4 K= 4		
0	95	94
2	-33	-25
4	-38	-37
6	-33	6
8	83	92
10	-43	9
12	-46	6
H= 4 K= 5		
1	74	-75
2	315	-295
3	76	-70
4	52	-50
5	-41	43
6	230	221
7	-46	50
8	-45	42
9	-46	-46
10	169	-168
11	-49	-35
12	51	-52
13	-43	29
H= 4 K= 6		
0	72	79
1	-33	-23
2	-38	1
3	-39	10
4	143	-137
5	-35	29
6	-61	-27
7	-42	1
8	72	61
9	-44	-26
10	-40	33
11	-46	2
12	68	-65
H= 4 K= 7		
1	-40	-17
2	258	-258
3	-41	16
4	45	-36
5	-42	5
6	229	226
7	-44	17
8	-49	65
9	-31	-17
10	156	-164
H= 4 K= 8		
0	98	109
1	-47	-48
2	-38	17
3	-47	37
4	48	-51
5	-49	42
6	-30	-18
7	-41	-30
8	-52	65
H= 4 K= 9		
1	50	61
2	-53	-60
3	66	77
4	-31	-6
5	-52	-52
6	68	59
H= 5 K= 5		
0	136	119
2	-44	41
4	173	-173
6	-36	-26
8	61	53
10	-46	33
12	82	-99
H= 5 K= 6		
1	67	-65
2	84	77
3	77	-66
4	-28	13
5	-28	26
6	47	-52
7	48	42
8	-39	-4
9	-40	-40
10	-41	44
11	-48	-35
H= 5 K= 7		
0	46	-36
1	60	-59
2	-28	20
3	60	59
4	82	85
5	-29	56
6	-30	6
7	-40	-45
8	51	-49
9	-32	-48
H= 5 K= 8		
1	-39	-11
2	123	-118
3	-30	-26
4	-40	-10
5	-40	-3
6	114	106
7	-42	5
H= 5 K= 9		
0	160	-157
1	-51	-49
2	-32	-14
3	-42	41
4	101	118
H= 6 K= 6		
0	281	269
2	-42	14
4	207	-204
6	-49	-62
8	204	204
H= 6 K= 7		
1	-48	-43
2	49	-56
3	-39	-36
4	-30	-3
5	-40	38
6	66	50
7	-52	51
8	-43	10
H= 6 K= 8		
0	151	150
1	-50	-44
2	-46	3
3	-47	41
4	149	-162
5	-52	49
H= 7 K= 7		
0	-54	5
2	-41	14
4	-48	-17
6	-49	0
H= 7 K= 8		
1	-43	-42
2	127	-129

Table 4. *R for various classes of reflections in* $NaSn_2F_5$

Class	Number of observed reflections	R
$h = 2n$	107	0·0527
$k = 2n$	118	0·0538
$l = 2n$	157	0·0496
$h = 2n+1$	103	0·0595
$k = 2n+1$	92	0·0589
$l = 2n+1$	53	0·1012
$h, k = 2n$	75	0·0506
$h, l = 2n$	87	0·0476
$k, l = 2n$	85	0·0466
$h, k, l = 2n$	59	0·0448
$h, k = 2n;\ l = 2n+1$	16	0·1052
$h = 2n;\ k = 2n+1$	32	0·0587
$h = 2n;\ l = 2n+1$	20	0·1053
$k = 2n;\ l = 2n+1$	33	0·1013
$h = 2n+1;\ k = 2n$	43	0·0602
$h = 2n+1;\ l = 2n$	70	0·0522
$k = 2n+1;\ l = 2n$	72	0·0539
$h, k = 2n+1$	60	0·0590
$h, l = 2n+1$	33	0·0986
$k, l = 2n+1$	20	0·1012
$h, k = 2n+1;\ l = 2n$	44	0·0532
$h, k, l = 2n+1$	16	0·0999

Table 5. *Interatomic distances* < 3·5 Å *and bond angles in* $NaSn_2F_5$

Distance

Sn–F(1)	2·08 ± 0·02 Å	F(2)–F(2)	3·15 ± 0·04 Å
–F(1)	2·53 ± 0·02	–F(2)	3·20 ± 0·05
–F(1)	3·01 ± 0·02	–F(3)	2·87 ± 0·03
–F(2)	2·07 ± 0·02	–F(3)	3·00 ± 0·04
–F(2)	2·98 ± 0·02	–Na(1)	2·48 ± 0·02
–F(3)	2·22 ± 0·01	–Na(2)	2·21 ± 0·02
F(1)–F(1)	2·63 ± 0·05	F(3)–2 Sn	2·22 ± 0·01
–F(1)	2·73 ± 0·04	–2 F(1)	2·80 ± 0·02
–F(2)	2·78 ± 0·03	–2 F(2)	2·87 ± 0·03
–F(2)	2·91 ± 0·03	–2 F(2)	3·00 ± 0·04
–F(2)	2·99 ± 0·03	–Na(2)	2·42 ± 0·02
–F(2)	3·01 ± 0·03		
–F(3)	2·80 ± 0·02	Na(1)–4 F(1)	2·33 ± 0·02
–Na(1)	2·33 ± 0·02	–4 F(2)	2·48 ± 0·02
		–2 Na(2)	3·42
		Na(2)–4 F(2)	2·21 ± 0·02
		–2 F(3)	2·42 ± 0·02

Angle

F(1)–Sn–F(2)	89·3 ± 0·9°	F(1)–Sn–F(1)	68·9 ± 1·0°
F(1)–Sn–F(3)	81·2 ± 0·7	F(1)–Sn–F(2)	142·7 ± 0·7
F(2)–Sn–F(3)	84·1 ± 0·9	Sn–F(3)–Sn	134·4 ± 1·8
F(1)–Sn–F(2)	73·7 ± 0·8	Sn–F(1)–Sn	111·1 ± 1·0

See Figs. 3 and 4.

vibration and their orientation relative to the crystallographic axes. The pertinent information on these ellipsoids is given in Table 6.

A projection along the c axis of the contents of the unit cell is shown in Fig. 1. Note that there are open channels running through the crystal in two of the four quadrants of the unit cell.* These channels are lined by the tin atoms with a minimum Sn–Sn distance of 4·41 Å across the channel. In the other two quadrants there are channels lined by fluorine atoms but these channels contain the sodium atoms stacked linearly, $c/4$ apart.

It is interesting that in this compound sodium has both six- and eightfold coordination with fluorine. Fig. 2 shows a portion of the unit cell as viewed along [110]. This figure gives the environment of the tin atom and Na(2). Na(2) has six fluorine neighbors forming a slightly elongated octahedron. Fig. 3 is a projection along [100] of Na(1) and its eight neighbors, showing a distorted antiprism.

Fig. 4 shows the arrangement of the discrete Sn_2F_5

Table 6. *Thermal vibration ellipsoids in* $NaSn_2F_5$

Atom	Axis i	r.m.s. amplitude	B	Angles between ellipsoid axes and crystallographic axes α	β	γ
Sn	1	0·14 ± 0·01 Å	1·58 ± 0·10 Å^2	27 ± 20°	116 ± 21°	86 ± 11°
	2	0·13 ± 0·01	1·31 ± 0·13	65 ± 21	28 ± 21	78 ± 9
	3	0·17 ± 0·01	2·22 ± 0·10	99 ± 11	99 ± 8	13 ± 9
F(1)	1	0·14 ± 0·05	1·6 ± 1·1	41 ± 19	126 ± 31	106 ± 38
	2	0·25 ± 0·04	4·7 ± 1·4	50 ± 18	51 ± 16	64 ± 11
	3	0·09 ± 0·06	0·6 ± 0·8	95 ± 34	120 ± 29	31 ± 23
F(2)	1	0·20 ± 0·03	3·1 ± 1·0	27 ± 54	64 ± 57	85 ± 19
	2	0·17 ± 0·04	2·2 ± 1·2	115 ± 56	27 ± 55	101 ± 25
	3	0·07 ± 0·07	0·4 ± 0·7	100 ± 17	82 ± 24	13 ± 22
F(3)	1	0·24 ± 0·06	4·4 ± 2·3	46 ± 5	46 ± 5	77 ± 24
	2	0·19 ± 0·07	2·8 ± 2·1	135	45	90
	3	0·12 ± 0·06	1·0 ± 1·1	99 ± 17	99 ± 17	13 ± 24
Na(1)	1	0·02 ± 0·45	0·03 ± 1·4	0	90	90
	2	0·21 ± 0·07	3·4 ± 2·2	90	0	90
	3	0·17 ± 0·04	2·3 ± 1·0	90	90	0
Na(2)	1	0·22 ± 0·08	3·8 ± 2·8	45	45	90
	2	0·16 ± 0·09	1·9 ± 2·2	135	45	90
	3	0·05 ± 0·10	0·2 ± 0·8	90	90	0

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* A similar feature in an entirely different structure has been observed in $Zr(IO_3)_4$ (Larson & Cromer, 1961).

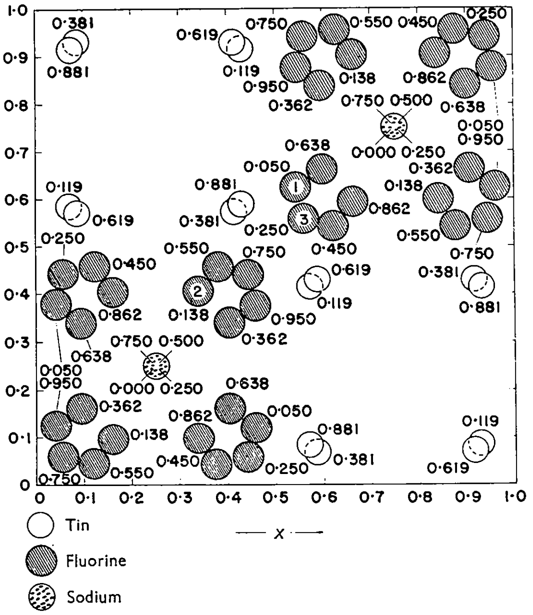

Fig. 1. A projection along the *c* axis of the contents of one unit cell of $NaSn_2F_5$.

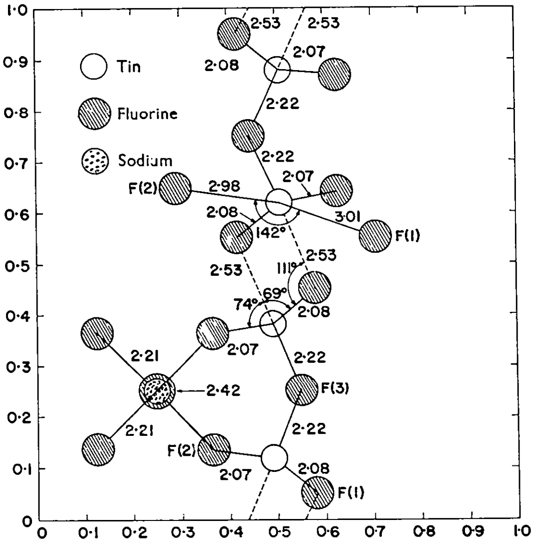

Fig. 2. A portion of the unit cell of $NaSn_2F_5$ as viewed along [110].

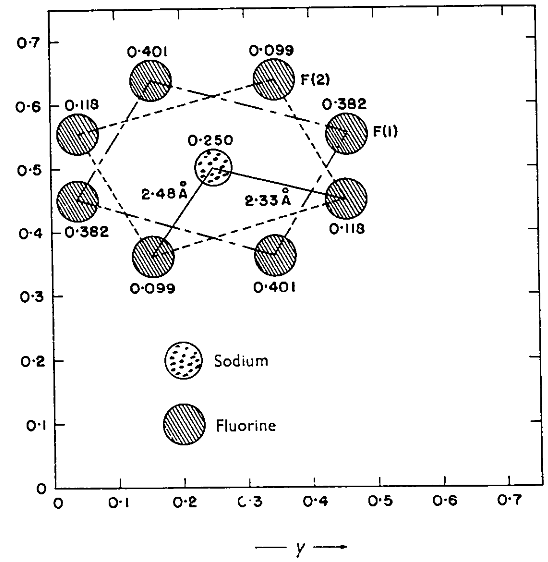

Fig. 3. Na(1) and its neighbors as viewed along [100].

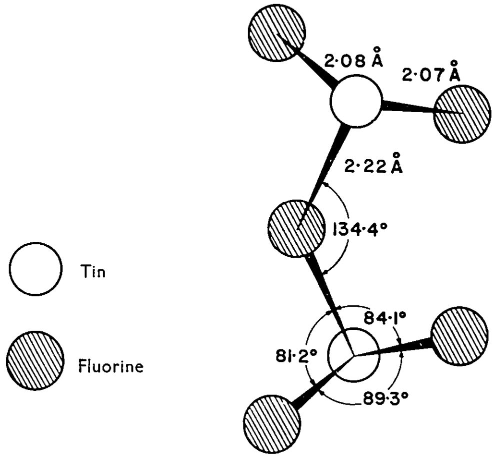

Fig. 4. The geometry of the Sn_2F_5 complex ion.

groups that exist in this compound. These complex ions have symmetry C_2 with the central atom, F(3), lying on a twofold axis. These ions are made up of two SnF_2 groups with covalent Sn–F bonds of 2·07 and 2·08 Å, and the two tin atoms are bridged by F(3). The Sn–F–Sn bonds in the bridge have a length of 2·22 Å, which is about midway between the values 2·06 Å expected for a pure covalent bond and 2·45 Å expected for a pure ionic bond. The Sn_2F_5 groups are linked together by weak Sn–F bonds of 2·53 Å to form infinite chains along the *c* axis.

The three-coordination of Sn(II) in this compound is similar to that observed in $SnCl_2$ and SnS (Rundle, 1962). The geometry suggests that the p^3 orbitals of the tin are being used. This can be rationalized by placing the extra electron on the bridging fluorine atom. This atom then alternately donates an electron pair to each tin to fill the third *p* orbital. The 2·22 Sn–F bond is thus a coordinate covalent bond. The bridging fluorine atom is somewhat analogous to a hydrogen atom in a hydrogen bond.

All calculations were made on an IBM 7090 computer, and the programs were written by the authors.

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