Herrn Dr H. J. Schönherr danken wir für seine Ratschläge und Diskussionsbeitrage. Der Deutschen Forschungsgemeinschaft danken wir für die Bereitstellung des Automatischen Einkristalldiffraktometers. Den Mitarbeitern des Instituts für Kristallographie danken wir für ihre Hilfe der Durchführung der experimentallen Arbeiten.

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The Crystal Structure of Ammonium Heptafluorothorate, Ammonium Catena-di-μ-fluoro-pentafluorothorate(IV)*

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(*Received* 29 *January* 1971)

Anhydrous $(NH_4)_3ThF_7$ is formed from $(NH_4)_3ThF_8$ upon equilibration with concentrated aqueous NH_4F solution (~36 wt.%). Its crystal structure was determined from counter measurenemts of 1053 reflections. Cell dimensions are a=13·944 (4), b=7·928 (2) and c=7·041 (4) Å, space group *Pnma*, Z=4, D_x=3·57, D_m=3·6 g.cm^{-3}. The structure was refined by full-matrix least-squares methods to an unweighted crystallographic R value of 0·042, with all atoms except hydrogen having anisotropic thermal parameters. The structure consists of chains parallel to the b axis in which thorium is nine-coordinated by fluorine atoms in a tricapped trigonal prism arrangement. Th–F distances span the range of 2·25 Å (unshared F) to 2·59 Å (shared F) with a mean value of 2·40 Å. The minimum F–F distance is 2·50 Å between bridging fluorine atoms; for unshared fluorine atoms the minimum F–F distance is 2·72 Å. Hydrogen positions were not found, but the N–F distances are normal for hydrogen bonding.

Introduction

Thorium is the largest of the tetravalent actinides and, indeed, is the largest of the M^{4+} ions. It is nine-coordinated in $(NH_4)_4ThF_8$ which is the highest complex known between NH_4F and ThF_4; in that compound one fluoride in the lattice is not bound to thorium (Ryan, Penneman & Rosenzweig, 1969). This is in contrast to the eight-coordination found in the isostoichiometric complexes $(NH_4)_4MF_8$ containing the next five smaller actinides, Pa^{4+} through Am^{4+}, whose structures contain isolated anions in the form of antiprisms (Rosenzweig & Cromer, 1970). Since in $(NH_4)_4ThF_8$ there is one fluoride coordinated only by ammonium ions, it was reasoned that loss of this NH_4F could yield the previously unknown compound $(NH_4)_3ThF_7$, which should be nine-coordinated with four fluorides shared between adjacent polyhedra. Thus, a search was made for it in the ThF_4–NH_4F–H_2O system. The comparable compound $(NH_4)_3UF_7$ is unknown in the analogous uranium system, even though specific attempts were made to prepare it (Penneman, Kruse, George & Coleman, 1964).

Experimental

In the search for $(NH_4)_3ThF_7$, samples of the 2:1 complex $(NH_4)_2ThF_6$ and the 4:1 complex $(NH_4)_4ThF_8$, were equilibrated separately with aqueous NH_4F of 20–40 wt.% concentrations. At room temperature, the higher complex (4:1) converts after several hours into small crystals of the desired 3:1 complex at 36 wt.%. NH_4F, but the very insoluble 2:1 complex does not convert completely even after three weeks in this medium. Larger crystals of the 3:1 compound of a size appropriate for a single-crystal study were obtained when a hot (80°C) solution of 36% NH_4F was saturated with $(NH_4)_4ThF_8$ (~1%), filtered through a plastic frit, and allowed to cool slowly, yielding plates charac-

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* Work performed under the auspices of the U. S. Atomic Energy Commission.

teristic of $(NH_4)_3ThF_7$. Analysis: (theory) NH_4F, 26·5%; Th, 55·4%; F, 31·7%; found: NH_4F, 26·1%; Th, 55·3%; F, 32·4%.

The flat plates of $(NH_4)_3ThF_7$ have {100} prominent and are commonly terminated by {011} and {120}. They show a low birefringence [$\alpha = 1{\cdot}492$, $\gamma = 1{\cdot}498$ with a very small $2V(-)$], in which separation of the isogyres is just perceptible (40 power, N.A. = 0·85 objective). Optic orientation is $Bxa = b$. Molar refractivity is 34·2 cm^3, within 3% of the value estimated from $(NH_4)_3ThF_7$ using the refractivities of $(NH_4)_4ThF_8$ and ThF_4, and 6·8 cm^3 as the empirical refractivity of NH_4F in fluoride complexes (Penneman, 1969).

Precession photographs of several crystals of $(NH_4)_3ThF_7$ using both a^* and c^* mounts, established orthorhombic symmetry. Reflections of the class $0kl$, $k+l=2n+1$, and $hk0$, $h=2n+1$ were systematically absent. Thus, the space group is either $Pnma$ or $Pn2_1a$. A flat with faces parallel to (100), about 0·04 mm thick by 0·15 × 0·08 mm in length and width, respectively, was used for data collection (b axis mount). Unit-cell dimensions obtained by least-squares refinement, based on the angle settings of 12 high-order reflections as determined on an automated Picker four-circle diffractometer using Mo $K\alpha_1$ ($\lambda = 0{\cdot}70930$ Å) radiation (take-off angle 2°), are $a = 13{\cdot}944$ (4), $b = 7{\cdot}928$ (2) and $c = 7{\cdot}041$ (4) Å. Zachariasen's (1948) volumes for NH_4^+ (26Å^3) and F^- (18 Å^3) indicated four molecules per cell and gave an estimated density of 3·4. The density calculated from the cell constants is 3·57 for $Z = 4$; pycnometric measurements using tetrabromoethane gave 3·6 g.cm^{-3}.

Intensity measurements were made on hkl and $h\bar{k}\bar{l}$ planes for which $2\theta \le 70°$, using a Picker computer-controlled four-circle diffractometer similar to that described by Busing, Ellison, Levy, King & Roseberry (1967). There were 343 data points taken singly, and 1294 averaged over two data sets. Zr-filtered Mo $K\alpha$ radiation, a two-degree θ–2θ scan, bisecting positions, and a take-off angle of 5°, were used to collect data. Of the 1637 reflections measured, 1053 were judged to be observed according to the criterion $(T-KB) \ge 3\sigma(I)$ where $\sigma(I) = (T+KB)^{1/2}$, T is the total count, and KB is the normalized background. The crystal was checked periodically for orientation and centering. Intensity of a standard reflection was sampled after every 30 reflections; it showed a 6·5% decrease over the period of data collection. Multiplicative correction factors for the data were derived by least-squares fitting the standard reflection measurements (as a function of time) with a fifth-order polynominal. The order of the polynominal was determined from significance tests based on the sum of the squares of the residuals (Hamilton, 1965). Standard corrections were made for Lorentz and polarization effects. An absorption correction was made by the Busing & Levy (1957) method using Burnham's program (1962), modified by Larson, Cromer & Roof (1964). The linear absorption coefficient for Mo $K\alpha$ radiation is 285·4 cm^{-1}, and the calculated transmission factors varied from 0·17 to 0·33. Eight planes were used to define the crystal whose volume was calculated as 0·00048 mm^3.

Structure determination and refinement

The thorium-atom position was determined from the Patterson function and placed in 4(c) of space group $Pnma$ (No. 62) with parameters $x \simeq 0{\cdot}06$, $y = \frac{1}{4}$, $z \simeq 0$. After some least-squares refinement, coordinates were $x = 0{\cdot}066$, $y = \frac{1}{4}$, $z = 0{\cdot}016$ and gave an unweighted $R = 0{\cdot}15$. A difference Fourier map, phased on the thorium atom, located reasonable positions for the nitrogen and fluorine atoms in the structure.

A full-matrix least-squares refinement of all non-hydrogen positions was carried out with Larson's (1970) programs using all observed reflections. This refinement included anisotropic temperature factors and an extinction parameter. The quantity minimized was $\sum w(F_o - F_c^*)^2$ where w is the weight based on counting statistics (Evans, 1961), and

$$F_c^* = KF_c \Big/ \left\{1 + g\,\mathrm{Lp}\left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right] F_c^2\right\}^{\frac{1}{2}}$$

in which K = scale constant, g = extinction correction (Zachariasen, 1963; Larson, 1967), Lp = Lorentz–polarization factor, and F_c = structure factor calculated in the usual way. Form factors used were those of Cromer & Waber (1965) for the thorium atoms; nitrogen and fluorine form factors were taken from *International Tables for X-ray Crystallography* (1962), and the dispersion terms for thorium ($\Delta f' = -8{\cdot}127$; $\Delta f'' = 8{\cdot}870$) were taken from Cromer's (1965) work.

The structure refined in $Pnma$ to a weighted R' value of 0·015 where $R' = \sum w^{\frac{1}{2}} \big| |F_o| - |F_c^*| \big| / \sum w^{\frac{1}{2}} |F_o|$. Unweighted R was 0·042. The low R value for the centric structure and the physically reasonable anisotropic temperature factors were taken as proof that the model and choice of space group were correct. Hamilton's (1965) tests on the sum of the squares of the residuals reject the hypothesis that extinction is not present and also the hypothesis that only the heavy atoms vibrate anisotropically, at the 0·001 confidence level. Final coordinates and anisotropic temperature factors are listed in Tables 1 and 2. Table 3 lists calculated and observed structure factors.

Table 1. *Fractional atomic coordinates*

Numbers in parentheses are the least-squares standard error and refer to the least significant digits.

		x	y	z
N(1)	4(c)	0·2787 (9)	0·25	0·4550 (16)
N(2)	8(d)	0·3810 (5)	0·0444 (8)	0·9997 (13)
Th	4(c)	0·06580 (4)	0·25	0·01241 (7)
F(1)	4(c)	0·9488 (7)	0·25	0·7809 (10)
F(2)	4(c)	0·6593 (6)	0·25	0·7483 (12)
F(3)	4(c)	0·5596 (7)	0·25	0·1517 (9)
F(4)	8(d)	0·1885 (5)	0·0788 (7)	0·1172 (7)
F(5)	8(d)	0·9464 (5)	0·0505 (6)	0·1306 (6)

Discussion

The structure consists of chains of nine-coordinated thorium atoms coordinated by fluorine atoms in a tricapped trigonal prism arrangement. The chains run parallel to the b axis; Fig. 1 shows a stereo view inclined 10° to the c axis. Thorium is located at $y=0{\cdot}25$ on the mirror plane which bisects the top and base triangles

Table 2. *Thermal parameters* ($\times 10^4$)

Defined as $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\right]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	27 (8)	51 (18)	100 (32)	0	−32 (25)	0
N(2)	19 (4)	62 (11)	75 (13)	−3 (12)	−25 (21)	69 (39)
Th	9·4 (2)	36·4 (6)	32·8 (8)	0	−0·5 (17)	0
F(1)	28 (6)	68 (13)	63 (15)	0	−32 (18)	0
F(2)	38 (8)	68 (14)	78 (16)	0	−58 (19)	0
F(3)	19 (5)	44 (11)	72 (14)	0	−9 (19)	0
F(4)	25 (4)	67 (10)	105 (11)	43 (12)	−36 (12)	4 (20)
F(5)	21 (4)	57 (9)	64 (9)	−11 (11)	28 (12)	−5 (16)

Table 3. *Observed and calculated structure factors*

Column headings are: h, $|F_o|/k$ and $|F_c{}^*|$.

h	$\lvert F_o\rvert/k$	$\lvert F_c{}^*\rvert$
K= 0 L= 0		
0	0	668
2	217	203
4	53	44
6	206	201
8	288	290
10	140	143
12	-33	14
14	131	132
16	151	155
18	65	66
20	-42	37
K= 0 L= 1		
1	247	235
2	24	24
3	88	87
4	21	19
5	42	51
6	37	41
7	264	267
8	-22	17
9	212	205
10	-27	24
11	31	28
12	-30	3
13	96	101
14	-33	19
15	145	146
16	-35	5
17	93	92
18	-37	15
19	-38	1
20	-39	3
21	64	60
K= 0 L= 2		
0	257	256
1	33	34
2	142	148
3	38	33
4	40	37
5	47	44
6	202	201
7	21	12
8	174	172
9	40	40
10	74	71
11	-30	5
12	-32	30
13	-32	7
14	132	131
15	-35	0
16	122	130
17	46	27
18	48	46
19	-40	9
20	49	49
K= 0 L= 3		
1	168	160
2	57	59
3	104	100
4	24	22
5	106	105
6	-20	13
7	200	199
8	-24	5
9	147	146
10	55	53
11	-31	27
12	-33	15
13	120	120
14	-35	10
15	129	130
16	-38	17
17	75	74
18	-40	27
19	-41	1
20	-43	17
K= 0 L= 4		
0	192	192
1	29	27
2	131	133
3	68	71
4	51	49
5	55	55
6	145	149
7	-25	25
8	123	120
9	35	34
10	90	87
11	56	50
12	39	38
13	37	36
14	120	116
15	-38	9
16	99	96
17	-41	28
18	44	43
19	-43	28
K= 0 L= 5		
1	152	148
2	44	42
3	87	87
4	117	116
5	87	86
6	47	50
7	157	157
8	-28	6
9	133	132
10	42	42
11	-34	26
12	56	55
13	91	94
14	-38	32
15	102	102
16	-42	9
17	72	66
18	-43	28
K= 0 L= 6		
0	169	169
1	28	23
2	145	127
3	117	119
4	-21	20
5	102	102
6	134	134
7	-30	25
8	129	130
9	-34	23
10	71	73
11	79	78
12	-38	20
13	64	64
14	79	89
15	-41	11
16	108	98
17	-43	25
K= 0 L= 7		
1	119	120
2	66	66
3	53	47
4	102	100
5	56	52
6	39	42
7	125	121
8	-34	3
9	106	107
10	63	63
11	-38	13
12	77	72
13	60	62
14	-43	25
15	95	84
K= 0 L= 8		
0	153	151
1	36	23
2	81	83
3	70	69
4	-34	20
5	50	56
6	79	81
7	-36	10
8	112	110
9	-45	38
10	60	58
11	67	64
12	-42	16
13	-44	38
K= 0 L= 9		
1	96	96
2	51	53
3	-37	36
4	76	75
5	43	35
6	-40	42
7	104	97
8	-41	17
9	69	67
10	61	58
11	-45	10
K= 0 L= 10		
0	76	75
1	-37	33
2	54	50
3	64	68
4	-40	12
5	62	59
6	65	59
7	-44	23
8	50	62
K= 0 L= 11		
1	56	45
2	59	55
3	-43	20
4	63	61
5	-46	28
K= 1 L= 0		
2	217	219
4	217	215
6	147	144
8	-21	22
10	200	196
12	169	163
14	66	71
16	46	52
18	106	112
20	92	93
K= 1 L= 1		
0	31	29
1	109	116
2	-15	14
3	237	238
4	19	17
5	176	177
6	38	36
7	59	54
8	32	33
9	127	121
10	-27	5
11	171	169
12	-30	3
13	115	117
14	-34	13
15	-34	15
16	-35	20
17	90	93
18	-38	3
19	106	106
20	-40	4
K= 1 L= 2		
1	36	33
2	161	167
3	22	20
4	279	275
5	17	12
6	158	160
7	36	36
8	36	33
9	-25	16
10	162	161
11	-29	3
12	161	159
13	-32	9
14	80	80
15	-35	21
16	39	43
17	-38	11
18	104	103
19	-40	3
20	84	86
K= 1 L= 3		
0	149	145
1	100	99
2	34	35
3	268	269
4	-16	3
5	224	223
6	31	32
7	58	58
8	79	75
9	91	95
10	35	38
11	180	177
12	-32	4
13	132	134
14	-36	31
15	-36	20
16	-38	30
17	78	77
18	-40	16
19	102	104
20	42	6
K= 1 L= 4		
1	91	88
2	149	145
3	28	25
4	200	193
5	27	24
6	96	98
7	78	80
8	-26	18
9	53	54
10	139	139
11	-31	17
12	147	144
13	-35	28
14	44	50
15	42	42
16	41	40
17	-41	30
18	90	89
19	-43	4
K= 1 L= 5		
0	39	38
1	67	67
2	31	33
3	176	176
4	-24	2
5	149	147
6	57	61
7	30	30
8	36	42
9	80	80
10	-31	15
11	137	137
12	-34	12
13	95	96
14	-40	46
15	-40	7
16	54	35
17	65	64
18	-46	11
K= 1 L= 6		
1	62	63
2	114	112
3	-27	26
4	175	173
5	38	41
6	101	103
7	64	67
8	33	28
9	44	44
10	109	109
11	-35	13
12	120	117
13	45	43
14	54	54
15	47	48
16	-45	30
17	50	29
K= 1 L= 7		
0	93	93
1	58	60
2	56	55
3	125	125
4	-30	8
5	108	110
6	54	59
7	38	28
8	70	68
9	56	62
10	44	45
11	103	99
12	-38	14
13	78	76
14	57	51
15	-43	7
K= 1 L= 8		
1	76	77
2	90	90
3	36	28
4	101	99
5	-39	34
6	68	68
7	76	76
8	-37	16
9	57	59
10	84	84
11	-40	16
12	95	84
13	-44	36
K= 1 L= 9		
0	92	86
1	49	44
2	54	53
3	87	86
4	-37	3
5	79	76
6	68	66
7	-40	20
8	75	76
9	54	49
10	-42	39
11	75	71
K= 1 L= 10		
1	68	73
2	52	50
3	-48	22
4	65	70
5	-47	34
6	52	47
7	69	69
8	-46	16
K= 1 L= 11		
0	71	73
1	-47	29
2	-46	43
3	65	62
4	-46	8
5	56	58
K= 2 L= 0		
0	258	255
2	178	182
4	18	6
6	195	192
8	218	217
10	136	130
12	57	55
14	152	151
16	102	111
18	47	50
20	-41	37
K= 2 L= 1		
1	227	225
2	27	26
3	61	63
4	133	130
5	138	137
6	55	57
7	194	192
8	-27	6
9	120	124
10	-27	11
11	31	36
12	33	36
13	100	101
14	-34	28
15	138	135
16	-35	5
17	90	90
18	-38	7
19	-39	2
20	-40	11
K= 2 L= 2		
0	195	186
1	14	11
2	148	149
3	74	75
4	25	22
5	61	60
6	196	186
7	-25	7
8	188	195
9	-28	6
10	87	87
11	38	36
12	44	45
13	-31	28
14	130	134
15	-36	5
16	115	113
17	-38	5
18	-40	37
19	-41	14
20	-43	40
K= 2 L= 3		
1	265	262
2	51	50
3	60	63
4	72	70
5	109	111
6	23	15
7	206	208
8	-25	10
9	154	159
10	39	43
K= 2 L= 3		
11	40	41
12	48	49
13	80	80
14	-35	13
15	139	135
16	-38	9
17	94	97
18	-41	22
19	-41	3
K= 2 L= 4		
0	249	249
1	23	15
2	139	138
3	68	68
4	-21	3
5	46	47
6	132	131
7	-25	10
8	198	204
9	32	32
10	102	105
11	51	53
12	39	38
13	-35	29
14	113	110
15	-38	5
16	109	104
17	-42	26
18	45	41
19	-44	32
K= 2 L= 5		
1	201	201
2	37	31
3	51	50
4	60	58
5	80	84
6	28	28
7	164	167
8	-29	14
9	131	132
10	45	47
11	34	28
12	43	35
13	65	64
14	-38	21
15	110	113
16	-41	18
17	76	83
18	-44	37
K= 2 L= 6		
0	140	141
1	37	34
2	109	107
3	76	77
4	-28	2
5	57	59
6	121	123
7	-30	22
8	145	145
9	37	41
10	69	65
11	56	59
12	-38	34
13	43	39
14	91	96
15	-41	8
16	92	90
17	-45	34
K= 2 L= 7		
1	109	106
2	61	66
3	-31	39
4	67	65
5	67	70
6	43	42
7	96	97
8	-34	4
9	75	70
10	48	42
11	-38	10
12	54	56
13	67	58
14	-42	25
15	85	84
K= 2 L= 8		
0	95	97
1	33	29
2	71	72
3	67	69
4	-34	8
5	57	59
6	76	76
7	-37	17
8	98	94
9	41	40
10	58	52
11	57	57
12	-43	31
13	-45	39
K= 2 L= 9		
1	90	92
2	59	58
3	43	33
4	85	89
5	48	50
6	54	53
7	87	70
8	-40	13
9	68	67
10	69	54
K= 2 L= 10		
0	67	65
K= 2 L= 10		
1	42	38
2	55	55
3	77	80
4	-40	1
5	67	73
6	62	57
7	-43	20
8	66	69
K= 2 L= 11		
1	57	61
2	44	53
3	-43	19
4	67	68
K= 3 L= 0		
2	223	218
4	301	301
6	108	107
8	-24	11
10	160	153
12	185	186
14	73	76
16	-37	34
18	102	104
20	92	103
K= 3 L= 1		
0	71	67
1	36	42
2	16	16
3	242	241
4	-14	5
5	219	219
6	43	42
7	52	54
8	29	19
9	92	93
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K= 10 L= 7		
1	62	60
2	-43	35
K= 11 L= 0		
2	82	78
4	93	90
6	57	55
8	-42	18
K= 11 L= 1		
0	-37	11
1	44	38
2	-37	8
3	92	88
4	-38	1
5	85	75
6	-39	8
7	-41	24
8	-42	11
9	46	48
K= 11 L= 2		
1	-37	13
2	69	68
3	-38	2
4	97	97
5	-39	2
6	68	55
7	-40	14
8	-42	13
9	-42	11
K= 11 L= 3		
0	47	37
1	48	34
2	-38	13
3	91	93
4	-38	3
5	89	83
6	-41	14
7	-41	22
8	-42	25
9	-44	42
K= 11 L= 4		
1	-39	29
2	64	60
3	-40	9
4	88	82
5	-41	9
6	-42	43
7	-42	30
8	-44	12
K= 11 L= 5		
0	-39	25
1	-40	28
2	-41	17
3	79	72
4	-41	1
5	71	65
6	-43	26
K= 12 L= 0		
0	96	93
2	49	51
4	-40	2
6	60	60
K= 12 L= 1		
1	89	78
2	-40	10
3	-41	17
4	-41	16
5	44	36
6	-43	14
7	81	74
K= 12 L= 2		
0	93	75
1	-39	9
2	55	51
3	-40	13
4	-41	2
5	-42	11
6	58	62
K= 12 L= 3		
1	81	79
2	-40	18
3	-40	27
4	-42	16
5	-44	42
K= 12 L= 4		
0	67	72

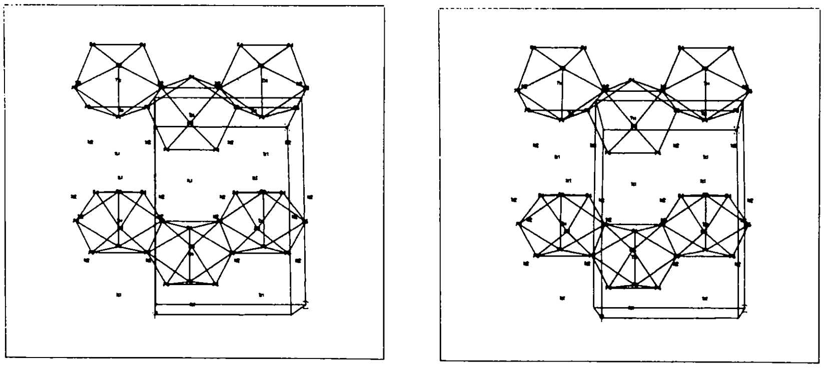

Fig. 1. Stereo view, inclined 10° to c axis.

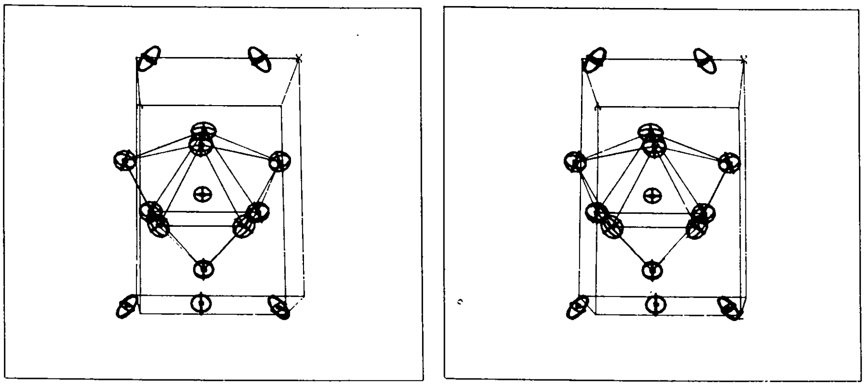

Fig. 2. Thermal ellipsoids (3 r.m.s. amplitudes) of fluorine and nitrogen atoms associated with one polyhedron.

of the trigonal prism. These triangles lie nearly in yz planes. Fig. 2 shows the thermal ellipsoids of the nine fluorine atoms associated with one polyhedron, together with those of nitrogen. Considering three adjacent polyhedra, the center one is situated so that two of its triangular-base fluorine atoms constitute face atoms of the two adjoining polyhedra. This arrangement opens the angle in the base to 65·43° and gives an F–F distance of 3·16 Å. In the opposite triangular face which contains three unshared fluorine atoms the corresponding angle is 55·04° with an F–F distance of 2·71 Å. In every polyhedron there are unshared fluorine atoms and four bridging fluorine atoms. Thus, the chains of $[ThF_7]_n^{3n-}$ are named catena-di-μ-fluoropentafluorothorate(IV). The four shared fluorine atoms are two corner atoms of a triangular prism base and two face atoms. Adjacent polyhedra are related by a center of symmetry between the shared fluorine atoms. Th–F distances span the range of 2·25 Å (closest unshared F) to 2·59 Å (shared F) with the mean = 2·40 Å. The minimum F–F distance at 2·50 Å occurs in a face-to-corner bridge; the only other F–F distances approaching contact distance are the unshared triangular base atoms at 2·71 Å. Table 4 summarizes some of the distances with the atoms numbered as in Fig. 3.

To date, the compound $(NH_4)_3ThF_7$ is apparently the only representative of the class of fluoride complexes between actinide tetrafluorides and NH_4F having this stoichimetry (3:1 NH_4F/MF_4). The comparable compound $(NH_4)_3UF_7$ was not found in the UF_4–NH_4F–H_2O system, although both $(NH_4)_4UF_8$ and $(NH_4)_2UF_6$ were easily prepared (Penneman *et al.*, 1964). For the slightly smaller lanthanide, Ce^{4+}, only the unstable hydrate $(NH_4)_3CeF_7.H_2O$ is found which disproportionates into the eight-coordinated com-

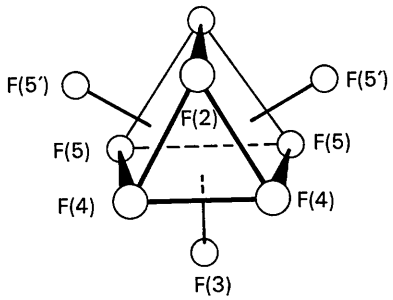

Fig. 3. Fluorine coordination polyhedron; atoms N(1), F(1), F(2), and F(3) lie on the mirror, $y=\frac{1}{4}$.

Table 4. *Interatomic distances* (Å)

Standard deviations are in parentheses.

Within tricapped prism (see Fig. 3)		
Th—F(1)		2·306 (9)
Th—F(2)		2·251 (8)
Th—F(3)		2·367 (6)
Th—F(4)	(2)	2·305 (6)
Th—F(5)	(2)	2·443 (6)
Th—F(5′)	(2)	2·592 (5)
F(2)–F(4)	(2)	2·938 (9)
F(4)–F(4)		2·715 (11)
F(1)–F(2)		2·942 (13)
F(4)–F(5)	(2)	3·385 (7)
F(1)–F(5)	(2)	2·927 (8)
F(5)–F(5)		3·164 (10)

N–F distances (≤3·0 Å)		
F(5)′–F(5)	(2)	2·502 (10)
F(5′)–F(1)	(2)	2·863 (7)
F(5′)–F(2)	(2)	2·921 (7)
F(5′)–F(4)	(2)	2·762 (9)
F(3)–F(5)	(2)	2·710 (8)
F(3)–F(4)	(2)	2·779 (9)
N(1)–F(2)		2·671 (14)
N(1)–F(4)	(2)	2·882 (7)
N(1)–F(5)	(2)	2·886 (11)
N(2)–F(1)		2·730 (10)
N(2)–F(2)		2·986 (9)
N(2)–F(3)		2·697 (8)
N(2)–F(4)		2·821 (10)
N(2)–F(5)		2·759 (10)

pounds $(NH_4)_2CeF_6$ and $(NH_4)_4CeF_8$ on dehydration (Penneman & Rosenzweig, 1969; Ryan, Larson & Kruse, 1969). The occurrence and stability of the nine-coordinated $(NH_4)_3ThF_7$ compound are attributed primarily to the larger size of Th^{4+}. The nearest-neighbor N–F distances are appropriate for hydrogen bonding, but hydrogen atoms were not included in the refinement.

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