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The Crystal Structure of α-KTh_6F_{25}, a Polymorph of CsU_6F_{25}*

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Crystals of α-KTh_6F_{25} are hexagonal-rhombohedral, $R\bar{3}m$, with hexagonal axes $a_0=8\cdot313$ (2), $c_0=25\cdot262$ (4) Å, $Z=3$ and $\varrho(\mathrm{cal})=6\cdot281$ g.cm^{-3}. Structural units of α-KTh_6F_{25} are identical to those of CsU_6F_{25} and comprise two adjacent rings of Th^{4+}–F polyhedra, 6 polyhedra per ring, with an alkali metal ion centered between the rings. The structural units are stacked *ABCABC* along c_0 in α-KTh_6F_{25} and *ABAB* in CsU_6F_{25}. K–F distances are 3·19 (2) and 3·20 (3) Å. Th–F distances range from 2·308 (1) to 2·541 (9) Å.

Introduction

Compounds exist with the stoichiometry $MF.6AF_4$, where M = K, Rb and Cs, and A = Th and U. Zachariasen (1948) published lattice parameters and the space group ($P6_3/mmc$) for KTh_6F_{25} and KU_6F_{25}, although Asker, Segnit & Wylie (1952) in their work on molten salt system KF–ThF_4 and Thoma, Insley, Landau, Friedman & Grimes (1958) in their work on system KF–UF_4 did not find an equilibrium compound at KF.6ThF_4 or at KF.6UF_4. Equilibrium relationships of $MF.6AF_4$ compounds were first established by Thoma *et al.* (1958) in their investigation of the RbF–UF_4 system and later by Thoma & Carleton (1961) in their study of system CsF–ThF_4. Unpublished work by Thoma and co-workers has established the existence of the remaining complex fluorides (Table 1).

Table 1. *Isomorphous* $MF.6AF_4$ *compounds*

$P6_3/mmc$	$R\bar{3}m$
CsU_6F_{25}	α-KTh_6F_{25}
$CsTh_6F_{25}$	$RbTh_6F_{25}$
RbU_6F_{25}	
KU_6F_{25}	
KTh_6F_{25}	

Brunton (1971) determined the structure of CsU_6F_{25} ($P6_3/mmc$), and Table 1 shows the compounds with this structure. The structure of α-KTh_6F_{25} has one isomorph, $RbTh_6F_{25}$, for which an erroneous space group was given by Brunton, Insley, McVay & Thoma (1965). Although the phase equilibrium work is not complete for all MF–AF_4 salt systems, the list in Table 1 is probably exhaustive.

Experimental

The compound α-KTh_6F_{25} was grown as primary phase crystals from a molten salt ingot of the composition KF–ThF_4 (20–80 mole%). A crystal ground to ellipsoidal shape (0·156 × 0·156 × 0·182 mm) was mounted on a computer-operated Picker four-circle goniostat, equipped with a scintillation counter detector. Conditions for reflections, $hkl, -h+k+l=3n$ and the diffraction symmetry $\bar{3}m$, are consistent with space groups $R\bar{3}m$, $R3m$ and $R32$. The solution of the structure was accomplished in $R\bar{3}m$.

Independent reflections were measured by the θ–2θ scan technique using unfiltered Ag $K\alpha$ radiation. Each reflection was step-scanned at intervals of 0·01° with a 2-sec count at each step for a total of 0·5° 2θ. The background was counted for 60 sec on each side of the peak. Take-off angle was 1·5°, and the total range of 2θ for reflections was 3–50°. A standard reflection (060) was measured every 20 reflections to monitor X-ray source variations. The range of net count for (060) was 21855 to 22954.

Lattice parameters were determined by a least-squares adjustment of 12 Ag $K\beta$ (0·49701 Å) reflections between 29 and 38° 2θ. At 24°C, $a_o=8\cdot313$ (2) and $c_o=25\cdot262$ (4) Å, $Z=3$ and $\varrho(\mathrm{cal})=6\cdot281$ g.cm^{-2}. Independent reflections were corrected for Lorentz and polarization effects and absorption ($\mu=461\cdot2$ cm^{-1}, correction range 0·0156–0·0322).

Starting parameters for Th and K were determined from sections of the three-dimensional Patterson function. When the relationship between the $P6_3/mmc$ and $R\bar{3}m$ structures became evident, atomic parameters for the F ions were estimated from the $P6_3/mmc$ (CsU_6F_{25}) structure (Table 2). The structure was refined by iterative least-squares adjustment using a modification of the Busing, Martin & Levy (1962) computer program. The quantity minimized by the least-squares program was $\sum w||F_o^2|-|F_c^2||^2$ with weights, w, equal to the reciprocals of the variances, which were estimated from the empirical equation:

$$\sigma^2(F_o^2)=\{T+B+[0\cdot05(T-B)]^2\}/\{A(\mathrm{Lp})^2\},$$

where T = total counts, B = background, counts A = absorption correction, and Lp = Lorentz and polarization corrections (Brown & Levy, 1964). Scattering factors for the ions were taken from Cromer & Waber (1965), and the anomalous dispersion terms for Th and K for

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Ag $K\alpha$ radiation were taken from Cromer (1965). Anisotropic temperature factors were calculated for Th^{4+} and K^+, and the temperature factors for F^- were constrained to be isotropic. Final parameters were calculated using data greater than $\sigma^2(F_o^2)$. Discrepancy indices are:

Table 2. *Atomic parameters of* α-KTh_6F_{25} *and* CsU_6F_{25}

	α-KTh_6F_{25}			CsU_6F_{25}		
	x	y	z	x	y	z
K–Cs	0	0	0	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$
Th–U	0·50031 (7)	$-x$	0·09135 (3)	0·1737	$2x$	0·11146
F(1)	$\frac{1}{2}$	0	0	0·184	$2x$	$\frac{1}{4}$
F(2)	0·193 (2)	$-x$	−0·0630 (8)	0·485	$2x$	0·144
F(3)	0·323 (2)	0	$\frac{1}{2}$	0·678	0	0
F(4)	0	0	0·208 (2)	$\frac{1}{3}$	$\frac{2}{3}$	0·068
F(5)	0	0	0·449 (2)	0	0	0·076
F(6)	0·141 (2)	$-x$	−0·3963 (9)	0·121	$2x$	0·649

α-KTh_6F_{25} temperature factors

	β_{11}†	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0·001 (2)	β_{11}	0·0001 (2)	$\frac{1}{2}\beta_{11}$	0	0
Th	0·0020 (2)	β_{11}	0·00008 (1)	0·0011 (1)	0·00002 (1)	$-\beta_{13}$
F(1)	0·0053 (3)					
F(2)	0·0079 (3)					
F(3)	0·0025 (2)					
F(4)	0·0041 (4)					
F(5)	0·0025 (3)					
F(6)	0·0092 (3)					

Isotropic βs for F; $\beta_{22}=\beta_{11}$, $\beta_{33}=c^{*2}\beta_{11}/a^{*2}$, $\beta_{12}=b^*\cos\gamma^*\beta_{11}/a^*$, $\beta_{13}=\beta_{23}=0$. a^*, b^*, c^* and γ^* are the reciprocal lattice parameters.

† Coefficients in the temperature factor:

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

Standard errors in parentheses, corresponding to the last significant digit, are given by the variance–covariance matrix.

Table 3. *Interatomic distances* (Å) for α-KTH_6F_{25}

6[K—F(6)]	3·19 (2)	6[K—F(2)]	3·20 (3)
Th—F(1)	2·308 (1)	2[Th—F(3)]	2·330 (4)
2[Th—F(2)]	2·34 (1)	2[Th—F(6)]	2·35 (1)
Th—F(4)	2·481 (7)	Th—F(5)	2·541 (9)
4[F(1)–F(2)]	2·74 (2)	4[F(1)–F(6)]	2·75 (2)
F(2)—F(4)	2·56 (3)	2[F(2)–F(6)]	2·77 (2)
2[F(3)–F(3)]	2·69 (2)	[F(5)—F(6)]	2·43 (3)
F(5)—F(5)	2·58 (6)		

Comparable cation–anion distances (Å) for CsU_6F_{25}

6[Cs—F(2)]	3·12 (2)	6[Cs—F(6)]	3·45 (4)
2[U—F(3)]	2·267 (8)	U—F(1)	2·279 (2)
2[U—F(6)]	2·29 (5)	2[U—F(2)]	2·29 (2)
U—F(4)	2·39 (4)*	U—F(5)	2·54 (6)

*Accidentally omitted from Table 2 (Brunton, 1971).

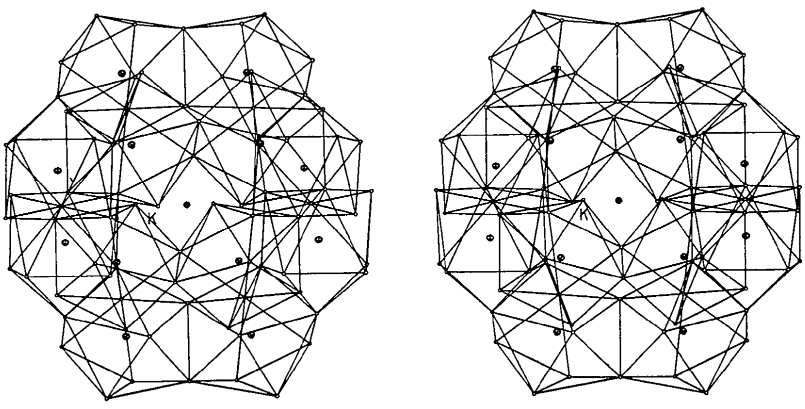

Fig. 1. One double ring of Th–F polyhedra with a central K ion. Ring tilted 30° about Cartesian y axis.

$$R_1=\sum||F_o^2|-F_c^2||/\sum|F_o^2| \;=0{\cdot}0802 \text{ for reflections } >\sigma$$
$$=0{\cdot}0834 \text{ for all 736 reflections.}$$
$$R_2=\sum||F_o|-|F_c||/\sum|F_o| \;=0{\cdot}0616 \text{ for 641 reflections } >\sigma$$
$$=0{\cdot}0782 \text{ for all reflections.}$$

The standard deviations of an observation of unit weight $[\sum w(F_o-F_c)^2/(n_o-n_v)]^{1/2}$ is 1·6024 where n_o is the number of reflections, 641, and n_v is the number of variables. Atomic parameters and temperature factors are listed in Table 2. Interatomic distances are given in Table 3. Observed and calculated structure factors are listed in Table 4. An extinction correction was applied to F_c by the method suggested by Zachariasen (1967, 1968); Zachariasen's $r^*=0{\cdot}00939$ (8).

Table 4. *Observed and calculated structure factors for* α-KTh_6F_{25}

L	FOBS	FCAL
	0 0 L	
3	95	-195
6	1025	-1025
3	414	394
12	1025	1032
15	609	-613
18	322	-416
21	741	756
24	613	358
27	823	-826
30	0	48
33	789	757
36	157	-118
	0 1 L	
2	138	-176
5	513	492
8	22	30
11	355	-367
14	113	108
17	326	311
20	94	-105
23	252	-237
26	212	203
29	201	196
32	234	-215
35	99	-68
38	235	237
	0 2 L	
1	952	952
4	723	-694
7	642	-602
10	1115	1055
13	489	487
16	1005	-976
19	16	-47
22	979	953
25	135	-108
28	731	-712
31	388	382
34	567	567
37	457	-446
	0 3 L	
0	266	-293
3	84	-120
6	581	545
9	115	-121
12	278	-259
15	131	152
18	291	273
21	295	-305
24	117	-22
27	244	244
30	40	45
33	265	-246
36	62	83
	0 4 L	
2	549	521
5	965	-917
8	0	-52
11	1108	1046
14	126	-119
17	873	-865
20	494	483
23	697	703
26	511	-519
29	392	-392
32	617	617
35	225	224
	0 5 L	
1	155	-175
4	231	239
7	169	148
10	325	-329
13	68	-67
16	381	362
19	67	80
22	305	-298
25	69	33
28	252	237
31	99	-62
	0 6 L	
0	1076	1053
3	158	-160
6	835	-784
9	436	402
12	791	766
15	571	-548
18	418	-402
21	623	638
24	304	319
27	621	-663
30	86	15
	0 7 L	
2	117	-127
5	324	294
8	107	89
11	261	-245
14	0	50
17	216	209
20	36	-63
23	159	-173
26	150	167
29	122	148
	0 8 L	
1	663	665
4	477	-470
7	441	-429
10	665	664
13	284	311
16	688	-663
19	0	-27
22	623	663
25	55	-88
	0 9 L	
0	224	-182
3	62	-13
6	250	272
9	85	-68
12	180	-167
15	131	120
18	199	176
21	190	-181
	0 10 L	
2	303	312
5	584	-584
8	100	-68
11	579	615
14	52	-54
	1 0 L	
1	372	-403
4	388	374
7	291	287
10	312	-337
13	100	-125
16	372	369
19	0	44
22	299	-296
25	208	84
28	281	265
31	141	-115
34	162	-160
37	175	166
	1 1 L	
0	365	-470
3	76	76
6	438	402
9	0	29
12	406	-405
15	288	291
18	208	195
21	244	-252
24	0	-77
27	303	308
30	61	-5
33	199	-207
36	51	50
	1 2 L	
2	66	-74
5	455	420
8	74	-82
11	350	-365
14	144	151
17	364	345
20	89	-112
23	264	-249
26	185	178
29	179	193
32	165	-192
35	74	-54
	1 3 L	
1	331	-362
4	342	314
7	287	258
10	287	-277
13	103	-118
16	348	326
19	0	34
22	258	-266
25	97	82
28	259	251
31	105	-112
34	157	-152
	1 4 L	
0	322	-348
3	85	78
6	354	318
9	73	-55
12	323	-310
15	261	261
18	167	174
21	229	-227
24	99	-68
27	254	273
30	0	-3
33	160	-183
	1 5 L	
2	111	-113
5	359	353
8	53	12
11	302	-278
14	91	85
17	272	268
20	116	-98
23	198	-188
26	180	168
29	117	163
32	176	-183
	1 6 L	
1	251	-270
4	243	239
7	214	205
10	225	-210
13	0	-91
16	252	259
19	0	21
22	190	-211
25	80	78
28	195	211
	1 7 L	
0	222	-227
3	86	74
6	226	232
9	120	-87
12	223	-227
15	275	227
18	136	160
21	186	-192
24	141	-71
27	209	222
	1 8 L	
2	102	-82
5	252	267
8	0	14
11	215	-208
14	36	67
17	196	210
20	118	-83
23	159	-141
	1 9 L	
1	195	-188
4	170	178
7	146	148
10	137	-163
13	84	-65
16	172	209
	1 10 L	
0	171	-179
3	12	56
6	183	185
9	0	-62
	2 0 L	
2	579	544
5	941	-936
8	68	-24
11	1176	1172
14	157	-168
17	932	-950
20	548	523
23	802	785
26	571	-557
29	428	-416
32	661	643
35	252	243
	2 1 L	
1	226	-262
4	352	322
7	211	186
10	359	-371
13	46	-90
16	396	401
19	0	68
22	322	-316
25	75	53
28	271	261
31	119	-88
34	188	-154
37	141	155
	2 2 L	
0	1172	1242
3	82	-42
6	1138	-1066
9	602	543
12	897	829
15	528	-513
18	530	-502
21	771	781
24	299	290
27	714	-715
30	0	-17
33	749	740
36	183	-146
	2 3 L	
2	184	-198
5	443	417
8	115	81
11	294	-281
14	0	44
17	262	260
20	57	-96
23	173	-188
26	151	186
29	169	181
32	214	-208
	2 4 L	
1	841	831
4	565	-577
7	555	-547
10	883	852
13	409	388
16	837	-806
19	67	-41
22	817	814
25	122	-111
28	615	-622
31	333	340
	2 5 L	
0	309	-317
3	95	38
6	322	304
9	40	-27
12	288	-275
15	205	198
18	187	166
21	180	-189
24	110	-67
27	239	248
30	0	9
	2 6 L	
2	403	384
5	755	-729
8	90	-96
11	848	824
14	117	-94
17	658	-661
20	384	367
23	532	565
26	424	-445
	2 7 L	
1	143	-174
4	180	179
7	128	143
10	205	-207
13	105	-75
16	260	263
19	0	56
22	223	-217
25	96	27
	2 8 L	
0	730	708
3	61	-76
6	652	-624
9	343	358
12	532	537
15	410	-397
18	350	-362
	2 9 L	
2	134	-98
5	230	221
8	34	46
11	176	-170
	3 0 L	
0	232	-292
3	71	-105
6	541	535
9	119	-134
12	231	-242
15	173	162
18	264	255
21	307	-310
24	77	20
27	258	245
30	42	34
33	252	-241
36	100	88
	3 1 L	
2	145	-154
5	449	420
8	69	55
11	324	-325
14	100	87
17	286	277
20	84	-95
23	218	-214
26	185	194
29	157	178
32	199	-202
35	0	-65
	3 2 L	
1	320	-344
4	306	280
7	313	285
10	259	-258
13	86	-103
16	303	276
19	0	32
22	264	-247
25	58	102
28	245	228
31	81	-113
34	161	-149
	3 3 L	
0	165	-185
3	61	-17
6	383	370
9	213	-174
12	233	-219
15	214	204
18	262	256
21	268	-282
24	67	-43
27	220	218
30	78	52
33	215	-207
	3 4 L	
2	59	-49
5	308	298
8	66	-24
11	297	-290
14	151	127
17	266	267
20	97	-89
23	206	-205
26	162	161
29	114	151
	3 5 L	
1	231	-247
4	225	208
7	216	218
10	221	-215
13	78	-79
16	230	241
19	0	37
22	220	-220
25	76	81
28	218	203
	3 6 L	
0	207	-194
3	0	16
6	307	290
9	124	-111
12	178	-166
15	175	156
18	153	175
21	214	-214
24	76	-17
	3 7 L	
2	72	-79
5	257	252
8	0	50
11	219	-216
14	69	65
17	175	186
20	99	-65
	3 8 L	
1	173	-155
4	150	163
7	108	141
10	183	-175
13	61	-43
16	198	197
	3 9 L	
0	164	-134
3	0	25
	4 0 L	
1	863	905
4	622	-619
7	598	-609
10	949	945
13	432	424
16	865	-863
19	51	-50
22	910	879
25	126	-123
28	685	-658
31	365	359
34	554	543
	4 1 L	
0	320	-348
3	67	63
6	370	326
9	0	-43
12	325	-323
15	239	252
18	193	190
21	207	-223
24	111	-82
27	268	273
30	0	9
33	193	-188
	4 2 L	
2	452	446
5	883	-838
8	0	-61
11	989	965
14	122	-120
17	788	-794
20	433	436
23	652	658
26	493	-488
29	351	-365
32	572	577
	4 3 L	
1	205	-221
4	231	238
7	123	153
10	271	-255
13	0	-92
16	316	325
19	11	53
22	269	-252
25	0	33
28	236	233
31	0	-76
	4 4 L	
0	913	893
3	101	-82
6	822	-779
9	452	439
12	685	653
15	472	-467
18	453	-429
21	601	643
24	238	263
27	567	-588
	4 5 L	
2	131	-122
5	274	282
8	98	59
11	230	-220
14	62	42
17	221	216
20	92	-69
23	179	-159
26	125	146
	4 6 L	
1	620	616
4	447	-424
7	429	-429
10	624	628
13	248	280
16	608	-600
19	26	-35
22	597	631
	4 7 L	
0	208	-206
3	0	28
6	184	216
9	0	-31
12	162	-190
15	122	148
	4 8 L	
2	290	273
5	548	-534
8	56	-70
	5 0 L	
2	88	-44
5	336	336
8	97	-98
11	295	-308
14	171	144
17	328	326
20	156	-111
23	227	-223
26	124	150
29	187	177
32	169	-166
	5 1 L	
1	237	-262
4	267	239
7	241	215
10	261	-258
13	80	-91
16	286	295
19	83	50
22	251	-254
25	79	67
28	218	229
31	74	-88
	5 2 L	
0	303	-317
3	94	64
6	311	291
9	0	-46
12	259	-252
15	212	213
18	118	140
21	168	-197
24	96	-43
27	223	247
30	0	-11
	5 3 L	
2	109	-130
5	340	325
8	94	45
11	257	-236
14	63	48
17	238	233
20	50	-87
23	165	-158
26	161	157
29	145	152
	5 4 L	
1	238	-216
4	194	206
7	183	180
10	181	-197
13	26	-66
16	217	227
19	0	22
22	196	-192
25	85	79
	5 5 L	
0	147	-191
3	102	67
6	210	205
9	34	-88
12	199	-206
15	240	214
18	152	159
21	169	-179
	5 6 L	
2	59	-63
5	234	237
8	0	-4
11	176	-184
14	105	70
17	177	195
	5 7 L	
1	214	-174
4	158	155
7	159	150
10	154	-150
	6 0 L	
0	990	1052
3	168	-158
6	828	-782
9	404	401
12	766	763
15	529	-548
18	418	-401
21	640	639
24	287	319
27	657	-664
30	0	14
	6 1 L	
2	125	-127
5	324	318
8	102	70
11	252	-257
14	0	57
17	228	228
20	56	-75
23	170	-177
26	142	169
29	98	154
	6 2 L	
1	724	744
4	520	-504
7	509	-492
10	713	697
13	337	346
16	684	-683
19	0	-25
22	679	693
25	131	-108
28	535	-555
	6 3 L	
0	198	-194
3	66	-13
6	316	300
9	99	-91
12	216	-183
15	151	143
18	181	196
21	207	-209
24	77	-36
	6 4 L	
2	320	332
5	652	-647
8	109	-55
11	710	710
14	60	-79
17	592	-503
20	324	332
	6 5 L	
1	97	-164
4	122	149
7	139	156
10	173	-176
13	116	-66
16	208	209
	6 6 L	
0	658	656
3	115	-99
6	546	-519
9	278	282
	7 0 L	
1	247	-264
4	256	239
7	175	191
10	0	-191
13	101	-89
16	227	245
19	42	9
22	208	-189
25	142	79
28	0	200
	7 1 L	
0	216	-227
3	75	61
6	259	237
9	140	-77
12	242	-235
15	208	220
18	172	171
21	153	-190
24	102	-82
27	206	223
	7 2 L	
2	0	-43
5	242	250
8	22	-23
11	236	-227
14	121	103
17	220	226
20	134	-84
23	202	-162
	7 3 L	
1	214	-213
4	178	188
7	177	166
10	177	-163
13	117	-86
16	222	224
19	0	24
22	135	-179
	7 4 L	
0	215	-206
3	45	58
6	221	204
9	0	-56
12	182	-168
15	174	165
	7 5 L	
2	47	-82
5	245	226
8	107	40
	8 0 L	
2	311	329
5	712	-669
8	107	-63
11	765	779
14	116	-107
17	640	-637
20	337	341
23	524	547
	8 1 L	
1	169	-196
4	181	173
7	208	176
10	241	-190
13	116	-75
16	207	227
19	0	48
22	185	-202
	8 2 L	
0	722	707
3	106	-73
6	640	-622
9	360	357
12	526	534
15	403	-397
18	339	-360
	8 3 L	
2	94	-92
5	205	232
8	58	32
11	155	-182
14	91	38
	8 4 L	
1	536	533
4	362	-363
7	359	-361
	9 0 L	
0	166	-182
3	106	20
6	298	257
9	56	-94
12	168	-142
15	103	138
18	70	146
21	175	-189
	9 1 L	
2	99	-86
5	234	236
8	111	49
11	205	-200
14	85	50
17	164	188
	9 2 L	
1	180	-153
4	192	159
7	144	138
10	148	-160
13	121	-40
	9 3 L	
0	132	-134
3	0	16
	10 0 L	
1	545	560
4	400	-371
7	449	-405
10	505	542
13	265	253
	10 1 L	
0	167	-179
3	0	36
6	173	191
9	97	

Results

The basic structural unit of α-$5Th_6F_{25}$ is a double ring of Th–F polyhedra, six polyhedra per ring, surrounding the K ion (Fig. 1). Each Th–F polyhedron is a capped trigonal prism with an F ion at each of the nine corners. Rings are joined by opposing polyhedra, sharing corners, F(1), as with CsU_6F_{25} (Brunton, 1971). The result is that each K is surrounded by 12F at distances of 3·19 (2) and 3·20 (3) Å. Within each ring the polyhedra link by sharing edges F(2)–F(4) and F(6)–F(5), alternately, and these are short F–F distances. Interatomic distances for both compounds are listed in Table 3 for comparison and to correct an omission in the original CsU_6F_{25} table. Th–F distances, except for Th–F(5) [2·541 (9) Å] are 0·03 to 0·1 Å longer than corresponding U–F distances. Cs–F distances are slightly longer than corresponding K–F distances.

The difference in the structures of α-KTh_6F_{25} and CsU_6F_{25} results from a different stacking arrangement for the double ring in each compound. The stacking order for CsU_6F_{25} along c_o is *ABAB* [$c_o=16{\cdot}78$ (2) Å] and the stacking order for α-KTh_6U_{25} is *ABCABC* $c_o=25{\cdot}262\ (2)\simeq\frac{3}{2}\ (16{\cdot}78)$ Å]. The stacking order should not be confused with hexagonal or cubic close-packing, because atoms within the structural units are not close-packed. Structures are illustrated in Fig. 2 & 3; the F polyhedra are omitted for clarity. Preliminary work by Thoma *et al.* (unpublished) indicates that the difference in the structures represents a polymorphic transition in the compound KTh_6F_{25}, and that the KTh_6F_{25} reported by Zachariasen (1948) is the low temperature or β-KTh_6F_{25} (CsU_6F_{25} form).

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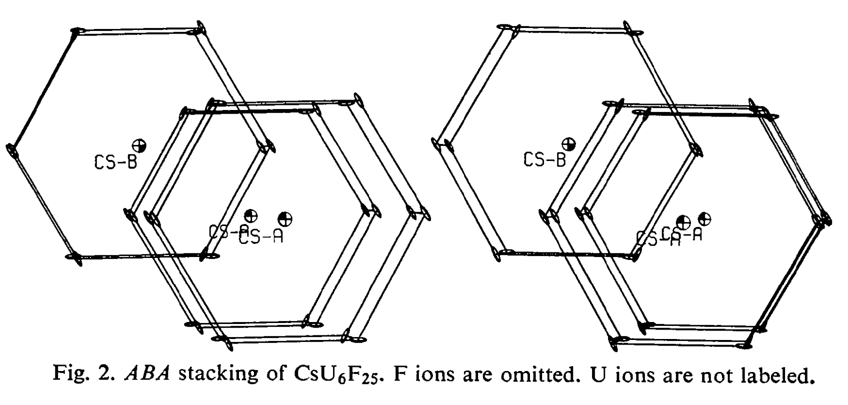

Fig. 2. *ABA* stacking of CsU_6F_{25}. F ions are omitted. U ions are not labeled.

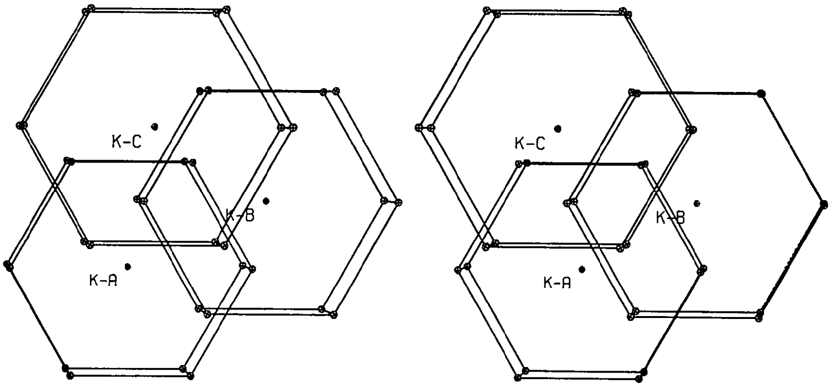

Fig. 3. *ABC* stacking of α-KTh_6F_{25}. F ions are omitted. Th ions are not labeled.

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The Crystal Structure of the Molecular Complex between Antimony Trichloride and Phenanthrene

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$2SbCl_3$.phenanthrene gives triclinic ($P\bar{1}$) crystals: $a = 8{\cdot}990(6)$, $b = 11{\cdot}10(1)$, $c = 10{\cdot}44(1)$ Å, $\alpha = 90{\cdot}7(1)$, $\beta = 80{\cdot}4(1)$, $\gamma = 69{\cdot}1(1)°$, $Z = 2$. The structure has been determined by three-dimensional Fourier methods and refined using block-diagonal least-squares down to $R = 3{\cdot}8$ %. The structure consists of alternating double layers of $SbCl_3$ and phenanthrene molecules. The coordination around Sb corresponds to a distorted trigonal bipyramid. Two independent Sb atoms are on opposite sides of the phenanthrene plane and their distances from that plane are not equal (3·27, 2·94 Å). The interactions between the metal atom and the aromatic molecule concern the π-electron system. Distorted octahedral coordination around the Sb atoms is completed by Sb···Cl contacts (3·260, 3·49, 3·41, 3·55 Å) significantly shorter than the sum of van der Waals radii.

Introduction

It is of interest to study the structure of the complexes formed by antimony trihalides with aromatic hydrocarbons, to determine the nature of the bonding interactions between the constituents and to obtain information on the mechanism of the catalytic effect which the antimony trihalides exert in Friedel–Crafts type reactions. The structure study of $2SbCl_3$.phenanthrene has been carried out to make a contribution to understanding the nature of the interactions between the inorganic and aromatic constituents, which could be related to the donor properties of the π system of phenanthrene and to the acceptor properties of $SbCl_3$. From the study of the pure quadrupole resonance spectrum of $2SbCl_3$.benzene, Okuda, Nakao, Shiroyama & Negita (1968) suggested that in this compound there is a charge transfer from the π system of benzene to a chlorine atom of $SbCl_3$, but a subsequent X-ray analysis carried out by Hulme & Szymanski (1969) showed that