The crystal structure

The structure consists of paired chains of molecules held together by van der Waals forces (Fig. 2). The planes of the molecules are at an angle of 55° to the (010) plane. In general the atoms lie, within experimental accuracy, on the best plane through the molecules (Table 3), but atoms Br, C(7) and N(2) appear to be displaced significantly from the plane, even at the rather large standard deviations obtained. With the exception of the angles in the cyclopentadiene ring at C(9), C(10) and C(13), where there is likely to be distortion from the values in fluorene, only three angles differ from the values in fluorene by more than two standard deviations. These are the angles at C(6), C(7) and C(8). Their standard deviations and temperature factors are no different from those of other atoms in the aromatic rings and there is no reason to suppose that any atom is misplaced. The distortion is presumably the result of interaction between atoms C(7) and Br in adjacent molecules. These atoms are separated by 3·86 Å which is the closest approach not involving hydrogen atoms between two adjacent molecules.

The only other difference of note between the geometry of this molecule and that of 2-bromoketofluorene (Griffiths & Hine, 1970) lies in the cyclopentadiene ring, where the bonds C(9)–C(10) and C(9)–C(13) are rather shorter in the present diazo compound than in the keto compound, and the angle C(10)–C(9)–C(13) is increased. These changes agree qualitatively with the calculations of Warren (1966). The accuracy of the present structure determination is, however, not great enough to establish the effect unequivocally.

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The Crystal Structure of $(NH_4)_4UF_8$*

By Abraham Rosenzweig† and Don T. Cromer
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544, *U.S.A.*

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The crystal structure of $(NH_4)_4UF_8$ has been determined from counter measurements of 849 reflections and refined by full-matrix least squares with anisotropic thermal parameters to an R index of 0·048. The space group is $C2/c$ with four formula units in a unit cell with $a = 13{\cdot}126 \pm 0{\cdot}005$, $b = 6{\cdot}692 \pm 0{\cdot}003$, $c = 13{\cdot}717 \pm 0{\cdot}005$ Å and $\beta = 121°19'$. The calculated density is 2·982 g.cm^{-3} and the measured density is 2·96 g.cm^{-3}. The uranium atom has 8 fluorine neighbors at an average distance of 2·28 Å which form a distorted tetragonal antiprism. These discrete polyhedra are linked *via* the ammonium ions, presumably through N–H---F hydrogen bonds. The four fluorine atoms nearest each nitrogen atom are roughly tetrahedrally disposed. The structure is compatible with the observed morphology and cleavage. The crystals usually twin on (001). There are several possible twinning mechanisms which result in a minimum distortion of the packing at the twin boundary. This compound is isostructural with analogous Pa, Am, Np and Pu compounds.

Introduction

Complexes of ammonium fluoride and actinide(IV) fluorides in the ratio 4:1 have been prepared for americium (Asprey & Penneman, 1962), neptunium (Keenan, 1963; Penneman, Kruse, George & Coleman, 1964), uranium and plutonium (Benz, Douglass, Kruse & Penneman, 1963) and protactinium (Asprey, Kruse & Penneman, 1967). On the basis of X-ray powder diffraction patterns, these compounds are considered to be isostructural. Additional data on the preparation of, and a description of $(NH_4)_4UF_8$ including partial optical properties are given by Penneman *et al.* (1964).

The only alkali-metal actinide(IV) fluoride of this stoichiometry thus far prepared is Li_4UF_8, whose structure has been described by Brunton (1967). This compound is orthorhombic with a distinctly different structure from that of the ammonium compounds.

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† Permanent address: Department of Geology, The University of New Mexico, Albuquerque, New Mexico, U.S.A.

$(NH_4)_4UF_8$, being reasonably stable in dry air and easily handled, was chosen for the determination of the structure of this class of compounds.

Experimental

Crystals for this study were prepared by R. A. Penneman by recrystallization from concentrated, aqueous NH_4F solution. The crystals are monoclinic diamond-shaped plates to short prisms. A large percentage of the crystals are in the form of simple twins on {001}. Morphological measurements were made with a two-circle reflecting goniometer, and the observed crystallographic forms were later indexed in accordance with the unit cell determined by X-ray diffraction. The most prominent forms are the pinacoid {001} and the prism $\{11\bar{1}\}$, modified by the prism {110} and the pinacoid {100}. A perfect cleavage occurs parallel to {001}. The idealized platy habit is shown in Fig. 1(*a*), and a typical short prismatic crystal is shown in Fig. 1(*b*).

The refractive indices for white light and the pleochroism are: $N_X = 1{\cdot}454$, pale yellow-green; $N_Y = 1{\cdot}459$, green; $N_Z = 1{\cdot}464$, deep blue-green. The optic angle is thus near 90° for white light, but strong, red > violet, crossed dispersion is observed. The orientation of the indicatrix is $X = b$, $Z \wedge a = 42°$ (623 mμ), 45° (530 mμ).

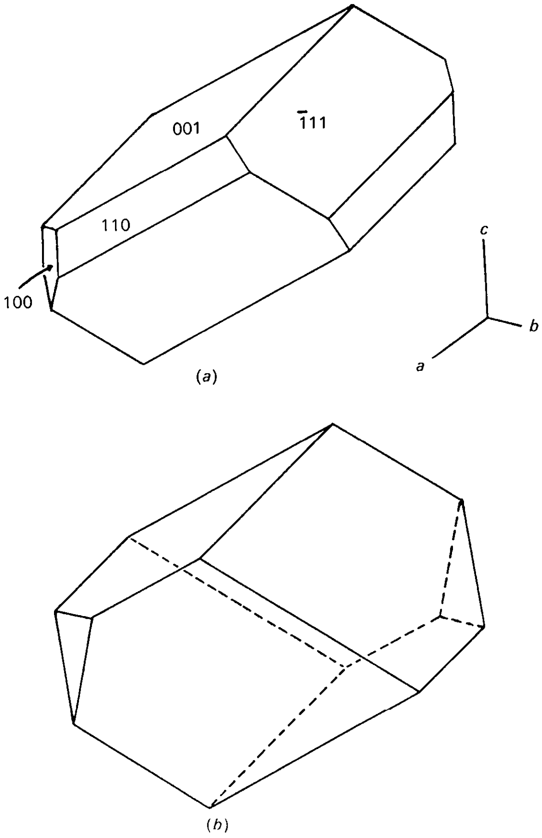


Fig. 1. (*a*) Idealized morphology of crystals of $(NH_4)_4UF_8$. (*b*) Morphology of the data crystal.

Precession photographs taken with Mo $K\alpha$ radiation of levels 0 to 3 with **b*** precessing, and of levels 0 to 4 with **c** precessing showed the following systematic absences: hkl absent if $h+k \neq 2n$, and $h0l$ absent if $h \neq 2n$ or $l \neq 2n$. The space group is thus *Cc* or *C*2/*c*, the latter choice being supported, though inconclusively, by the persistent centrosymmetric morphology. A further, non-systematic restriction is that reflections of the type $h3l$ with l odd are very weak or missing. Lattice constants (at room temperature, ~23°C) were obtained by a least-squares fit to the 2θ values of 30 high-order reflections measured using a single-crystal orienter on a General Electric Co. XRD-5 with Mo $K\alpha$, radiation ($\lambda = 0{\cdot}70926$ Å). The cell constants thus obtained are $a = 13{\cdot}126 \pm 0{\cdot}005$, $b = 6{\cdot}692 \pm 0{\cdot}003$, $c = 13{\cdot}717 \pm 0{\cdot}005$ Å, $\beta = 121°19{\cdot}3'$. The calculated density for four formula weights per unit cell is 2·982 g.cm^{-3}, in good agreement with the value 2·96 g.cm^{-3} measured by the pycnometer method (Penneman, 1966).

The crystal chosen for the collection of intensity data was a short prism elongated along the zone [101], and is illustrated in Fig. 1(*b*). The dimensions of the crystal were 0·14 × 0·13 × 0·06 mm. The crystal was coated with a thin film of fluorolube to protect it from the atmosphere. At the conclusion of the data collection procedure, the crystal was examined under the polarizing microscope and no indication of decomposition was noted. Intensities from a full hemisphere were measured to $2\theta \simeq 50°$ using Mo $K\alpha$ radiation with Zr–Y balanced filters and the fixed-counter, fixed-crystal technique. Of the 908 non-equivalent reflections in the hemisphere and within the 2θ limit, 849 were observed. Lorentz-polarization factors were applied in the usual way, and the absorption corrections (for the crystal bounded by eight planes) were applied by the Busing & Levy (1957) method using the program of Burnham (1962) modified for the present geometry. The linear absorption coefficient, μ, for Mo $K\alpha$ radiation is 235·5 cm^{-1}.

Determination of the structure

With four formulas per unit cell, the uranium atoms could be placed in the general positions of *Cc* or in one of several fourfold sets of *C*2/*c*. In the centric space group, two of the possible sets would place the uranium atoms in a body-centered array, and two other sets would place them in a face-centered array. Thus reflections with either $h+k+l=2n$ or reflections with $h,k,l,$ all odd or all even would in general be strong; neither of these cases agrees with the observed intensities. The remaining fourfold set, 4(*e*), of the centric space group places atoms at $\pm(0,y,\frac{1}{4})$ plus *C*-centering, and the general positions of the acentric space group are equivalent to it since the origin of the *a* and *c* axes is not fixed. The observation that reflections of the type $h3l$ with l odd are weak is satisfied by placing the uranium atoms in set 4(*e*) of $C2/c$ with $y\simeq\frac{1}{3}$ or $\frac{1}{6}$, the two values differing only in choice of origin.

A three-dimensional Patterson map confirmed the choice of placing the uranium atoms in the fourfold set 4(*e*) with $y\simeq\frac{1}{6}$. Neither the Patterson map nor the morphology suggest an acentric symmetry, and further solution of the structure was attempted in the centric space group. From this map the positions of three light atoms, assumed to be fluorines from their proximity to the uranium atoms, were assigned in three eightfold general sets. This model, with uranium and three-fourths of the total fluorine, gave an R value of 0·12.

A difference Fourier with F_o phased by the uranium atom and three fluorine atoms was calculated at this stage. The remaining light atoms, one fluorine and two

Table 1. *Final least-squares parameters for* $(NH_4)_4UF_8$

	x	y	z	$\beta_{11}\times 10^4$	$\beta_{22}\times 10^4$	$\beta_{33}\times 10^4$	$\beta_{12}\times 10^4$	$\beta_{13}\times 10^4$	$\beta_{23}\times 10^4$
U	0	0·1682 ± 2	$\frac{1}{4}$	25 ± 1	87 ± 2	19 ± 1		32 ± 1	
F(1)	0·0243 ± 9	0·0071 ± 18	0·1166 ± 9	66 ± 10	196 ± 30	56 ± 10	−34 ± 30	95 ± 17	−86 ± 30
F(2)	0·1597 ± 9	−0·0317 ± 18	0·3580 ± 9	52 ± 10	231 ± 35	56 ± 10	64 ± 29	75 ± 17	72 ± 30
F(3)	0·1599 ± 8	0·3237 ± 17	0·2528 ± 8	49 ± 9	145 ± 25	50 ± 9	−25 ± 28	74 ± 15	6 ± 29
F(4)	0·0784 ± 9	0·3952 ± 15	0·3921 ± 9	64 ± 10	166 ± 30	41 ± 9	−62 ± 26	70 ± 16	−74 ± 25
N(1)	0·3824 ± 12	0·1531 ± 24	0·3921 ± 12	46 ± 13	136 ± 39	44 ± 12	−15 ± 41	59 ± 22	−14 ± 41
N(2)	0·2115 ± 13	0·1111 ± 21	0·0836 ± 12	44 ± 13	132 ± 41	31 ± 12	−54 ± 34	47 ± 22	−28 ± 33

$g = 5{\cdot}3 \pm 1{\cdot}5 \times 10^{-8}$.

Table 2. *Observed and calculated structure factors for* $(NH_4)_4UF_8$

Column headings are l, F_o/K, $F_c{}^*/K$ (see text). A minus sign preceding F_o means 'less than'.

H= 0	K= 0	
2	303	-320
4	110	125
6	327	-326
8	285	283
10	152	-157
12	143	143
H= 0	K= 2	
0	65	-66
1	191	-188
2	169	169
3	159	165
4	232	-233
5	196	-199
6	137	135
7	150	155
8	74	-75
9	116	-112
10	84	87
11	114	119
12	92	-84
13	101	-101
H= 0	K= 4	
0	118	-120
1	182	180
2	79	84
3	129	-131
4	97	-95
5	115	113
6	115	118
7	131	-134
8	60	-62
9	126	127
10	44	44
11	93	-93
12	66	-66
H= 0	K= 6	
0	168	169
1	-22	5
2	160	-157
3	-23	7
4	139	137
5	-23	-9
6	138	-133
7	-25	8
8	133	128
9	-26	0
H= 1	K= 1	
-14	49	-43
-13	104	113
-12	72	75
-11	136	-145
-10	100	-106
-9	167	188
-8	70	73
-7	215	-215
-6	77	-74
-5	251	245
-4	147	136
-3	285	-275
-2	149	-147
-1	343	297
0	166	175
1	268	-284
2	129	-132
3	232	237
4	48	51
5	231	-238
6	98	-99
7	198	200
8	124	123
9	135	-134
10	75	-76
11	126	124
12	58	50
13	120	-115
H= 1	K= 3	
-13	-27	-10
-12	118	-124
-11	-24	16
-10	148	161
-9	-23	-5
-8	139	-137
-7	43	-14
-6	179	174
-5	-21	-2
-4	274	-272
-3	54	48
-2	207	201
-1	-21	-12
0	124	-130
1	28	-18
2	224	239
3	31	-31
4	242	-258
5	-20	5
6	159	159
7	26	16
8	125	-122
9	31	24
10	140	139
11	-25	-16
12	129	-126
H= 1	K= 5	
-11	100	107
-10	53	-51
-9	115	-121
-8	98	99
-7	108	109
-6	74	-72
-5	131	-130
-4	45	36
-3	175	172
-2	114	-109
-1	161	-167
0	116	124
1	131	139
2	56	-54
3	131	-135
4	56	60
5	130	136
6	90	-89
7	122	-116
8	77	74
9	104	98
10	55	-51
H= 1	K= 7	
-7	109	-98
-6	48	-39
-5	116	107
-4	50	43
-3	121	-114
-2	61	-55
-1	98	103
0	64	56
1	103	-100
2	55	-47
3	124	120
4	50	43
5	109	-105
H= 2	K= 0	
-14	144	-145
-12	142	142
-10	159	-170
-8	220	222
-6	233	-226
-4	268	256
-2	340	-299
0	269	301
2	240	-231
4	158	165
6	208	-219
8	206	207
10	118	-119
12	101	96
H= 2	K= 2	
-14	57	55
-13	120	117
-12	81	-79
-11	153	-153
-10	91	91
-9	156	152
-8	92	-91
-7	180	-173
-6	123	123
-5	284	279
-4	144	-139
-3	256	-236
-2	99	87
-1	122	138
0	89	-96
1	294	-297
2	159	163
3	285	290
4	134	-136
5	125	-130
6	59	63
7	143	145
8	60	-60
9	164	-165
10	82	81
11	109	104
12	69	-65
H= 2	K= 4	
-12	44	-47
-11	124	122
-10	76	74
-9	137	-135
-8	83	-82
-7	155	153
-6	72	71
-5	180	-176
-4	102	-98
-3	215	199
-2	91	92
-1	205	-206
0	71	-73
1	165	178
2	98	102
3	152	-155
4	86	-89
5	157	161
6	58	59
7	150	-149
8	59	-59
9	119	115
10	57	54
H= 2	K= 6	
-10	97	-94
-9	-27	10
-8	116	111
-7	37	-30
-6	149	-144
-5	-24	-2
-4	136	132
-3	26	10
-2	115	-119
-1	35	31
0	140	144
1	23	-13
2	143	-141
3	-22	-2
4	120	113
5	-23	-22
6	105	-105
7	30	6
H= 3	K= 1	
-15	116	-112
-14	92	-97
-13	113	111
-12	88	85
-11	103	-114
-10	57	-54
-9	200	192
-8	130	127
-7	196	-193
-6	206	-199
-5	96	101
-4	177	160
-3	246	-211
-2	158	-136
-1	279	274
0	140	146
1	134	-145
2	153	-157
3	146	149
4	126	129
5	175	-179
6	99	-100
7	128	133
8	97	95
9	107	-107
10	72	-69
11	105	101
H= 3	K= 3	
-14	122	119
-13	-28	-9
-12	148	-149
-11	28	17
-10	200	199
-9	39	34
-8	225	-223
-7	25	-11
-6	210	204
-5	72	-69
-4	259	-245
-3	-24	-10
-2	314	306
-1	64	59
0	252	-266
1	19	24
2	221	229
3	31	-16
4	214	-216
5	-21	-13
6	178	179
7	-22	-7
8	153	-151
9	-24	6
10	134	129
H= 3	K= 5	
-12	65	61
-11	83	82
-10	77	-74
-9	113	-111
-8	101	94
-7	127	123
-6	100	-105
-5	122	-115
-4	95	93
-3	136	141
-2	106	-103
-1	128	-133
0	121	122
1	96	98
2	87	-89
3	117	-117
4	76	77
5	125	123
6	94	-93
7	94	-92
8	70	66
H= 3	K= 7	
-7	91	-88
-6	51	-48
-5	100	99
-4	39	40
-3	75	-78
-2	50	-54
-1	98	92
0	62	59
1	118	-110
2	48	-46
3	78	79
4	46	39
H= 4	K= 0	
-14	149	-142
-12	138	140
-10	151	-150
-8	233	233
-6	278	-262
-4	236	212
-2	231	-229
0	197	208
2	208	-209
4	235	240
6	172	-166
8	118	112
10	137	-127
H= 4	K= 2	
-15	88	-94
-14	55	49
-13	154	156
-12	94	-89
-11	171	-169
-10	124	122
-9	148	149
-8	67	-69
-7	221	-217
-6	51	45
-5	269	251
-4	161	-145
-3	235	-217
-2	166	166
-1	236	242
0	87	-89
1	226	-236
2	77	82
3	184	187
4	92	-95
5	150	-153
6	60	80
7	137	134
8	72	-71
9	130	-123
10	64	62
H= 4	K= 4	
-13	105	-101
-12	68	-63
-11	172	137
-10	94	93
-9	163	-164
-8	77	-70
-7	138	159
-6	39	32
-5	192	-191
-4	88	-91
-3	208	210
-2	151	146
-1	160	-161
0	55	-59
1	150	155
2	42	34
3	174	-180
4	98	-99
5	153	149
6	75	73
7	110	-106
8	47	-34
9	95	93
H= 4	K= 6	
-10	102	-98
-9	-26	19
-8	115	111
-7	-25	0
-6	137	-136
-5	-24	0
-4	127	133
-3	32	-19
-2	107	-107
-1	28	19
0	122	123
1	25	-10
2	144	-140
3	-22	1
4	105	105
5	-24	-4
6	87	-82
H= 5	K= 1	
-15	114	-112
-14	87	-88
-13	143	141
-12	79	81
-11	170	-171
-10	41	-35
-9	178	174
-8	149	139
-7	222	-207
-6	271	-244
-5	275	242
-4	46	34
-3	233	-225
-2	37	16
-1	238	240
0	211	213
1	208	-218
2	165	-167
3	159	168
4	38	36
5	162	-162
6	61	-64
7	143	142
8	87	80
9	109	-106
10	59	-51
H= 5	K= 3	
-14	125	125
-13	-27	-4
-12	171	-173
-11	-26	-14
-10	171	169
-9	-25	-18
-8	159	-155
-7	37	33
-6	210	199
-5	-24	-1
-4	226	-221
-3	-20	-9
-2	212	219
-1	25	3
0	194	-202
1	25	22
2	145	150
3	32	-27
4	149	-147
5	23	-6
6	154	159
7	-23	5
8	124	-119
9	31	12
H= 5	K= 5	
-12	52	47
-11	99	98
-10	50	-70
-9	123	-121
-8	94	94
-7	144	145
-6	75	-74
-5	135	-135
-4	73	76
-3	111	114
-2	84	-84
-1	126	-129
0	70	71
1	140	142
2	81	-81
3	114	-120
4	71	73
5	102	97
6	48	-44
7	89	-84
H= 5	K= 7	
-7	98	-100
-6	65	-61
-5	100	101
-4	48	40
-3	103	-101
-2	48	-40
-1	107	101
0	66	59
1	97	-96
2	44	-46
H= 6	K= 0	
-16	142	152
-14	128	-138
-12	175	173
-10	268	-267
-8	278	266
-6	258	-246
-4	303	286
-2	273	-269
0	260	274
2	258	-263
4	186	183
6	148	-144
8	146	137
H= 6	K= 2	
-15	115	-117
-14	85	81
-13	122	121
-12	99	-97
-11	136	-128
-10	120	114
-9	146	144
-8	109	-106
-7	170	-164
-6	125	114
-5	177	178
-4	186	-175
-3	159	-158
-2	168	173
-1	155	161
0	82	-89
1	154	-159
2	75	81
3	114	115
4	116	-118
5	117	-117
6	100	96
7	124	120
8	59	-55
9	85	-80
H= 6	K= 4	
-14	43	37
-13	93	-92
-12	63	-65
-11	127	121
-10	101	111
-9	149	-149
-8	61	-55
-7	157	127
-6	54	48
-5	102	-111
-4	131	-139
-3	142	145
-2	108	110
-1	141	-147
0	47	-40
1	114	115
2	70	67
3	118	-116
4	86	-87
5	105	109
6	66	62
7	78	-79
H= 6	K= 6	
-10	113	-109
-9	-26	-7
-8	143	147
-7	29	-3
-6	135	-145
-5	-24	10
-4	120	121
-3	-24	-11
-2	136	-137
-1	-23	-1
0	146	145
1	27	8
2	118	-117
3	-24	8
4	105	99
H= 7	K= 1	
-16	49	53
-15	122	-125
-14	88	-84
-13	157	150
-12	82	75
-11	191	-191
-10	82	-77
-9	201	192
-8	120	111
-7	192	-186
-6	105	-97
-5	269	257
-4	72	69
-3	248	-248
-2	90	-92
-1	159	159
0	128	125
1	181	-181
2	94	-94
3	186	189
4	44	43
5	124	-124
6	55	-52
7	107	101
8	79	70
H= 7	K= 3	
-15	-29	6
-14	117	124
-13	-27	-10
-12	137	-137
-11	-26	0
-10	152	156
-9	-26	-11
-8	162	-158
-7	29	29
-6	165	169
-5	26	17
-4	200	-197
-3	-21	-17
-2	159	166
-1	50	-48
0	133	-133
1	25	19
2	150	151
3	30	23
4	142	-143
5	-23	7
6	109	109
7	-25	-14
H= 7	K= 5	
-12	72	74
-11	122	125
-10	64	-61
-9	127	-129
-8	54	55
-7	98	114
-6	74	-83
-5	127	-133
-4	74	75
-3	143	140
-2	68	-59
-1	120	-119
0	70	71
1	118	120
2	67	-65
3	107	-107
4	54	52
5	84	76
H= 7	K= 7	
-5	109	107
-4	51	49
-3	89	-84
-2	39	-35
H= 8	K= 0	
-16	109	111
-14	175	-178
-12	200	202
-10	165	-163
-8	191	187
-6	253	-227
-4	221	221
-2	204	-209
0	179	181
2	160	-158
4	143	139
6	116	-115
H= 8	K= 2	
-15	133	-135
-14	69	64
-13	100	135
-12	59	-60
-11	107	-102
-10	101	106
-9	186	182
-8	123	-127
-7	223	-222
-6	93	92
-5	130	128
-4	86	-80
-3	145	-148
-2	98	98
-1	194	197
0	91	-95
1	138	-139
2	78	78
3	117	114
4	74	-68
5	119	-119
6	64	59
7	83	92
H= 8	K= 4	
-14	55	55
-13	114	-118
-12	63	-57
-11	129	134
-10	76	75
-9	134	-133
-8	84	-89
-7	126	131
-6	72	68
-5	148	-148
-4	71	-69
-3	156	155
-2	85	82
-1	138	-137
0	64	-62
1	116	120
2	62	59
3	107	-105
4	68	-60
5	95	94
H= 8	K= 6	
-10	91	-103
-9	-26	1
-8	114	122
-7	-25	-4
-6	126	-127
-5	30	27
-4	114	109
-3	-24	0
-2	110	-107
-1	29	-8
0	103	114
1	33	-20
H= 9	K= 1	
-16	69	64
-15	102	-98
-14	98	-99
-13	133	131
-12	100	100
-11	128	-154
-10	71	-67
-9	133	136
-8	94	94
-7	152	-147
-6	141	-133
-5	166	160
-4	117	116
-3	138	-142
-2	102	-103
-1	124	131
0	79	82
1	125	-125
2	68	-64
3	113	114
4	83	76
5	97	-96
6	60	-65
H= 9	K= 3	
-14	117	122
-13	-28	8
-12	142	-146
-11	-27	-11
-10	201	205
-9	-26	-17
-8	197	-207
-7	-24	-7
-6	158	157
-5	-23	10
-4	174	-171
-3	32	20
-2	202	206
-1	-22	-5
0	164	-163
1	25	-11
2	129	126
3	28	1
4	132	-128
5	31	6
H= 9	K= 5	
-12	76	80
-11	99	101
-10	71	-70
-9	93	-100
-8	56	63
-7	96	96
-6	98	-93
-5	106	-108
-4	91	100
-3	116	114
-2	66	-59
-1	103	-93
0	58	57
1	74	74
2	83	-78
H= 10	K= 0	
-16	103	106
-14	148	-158
-12	173	187
-10	106	-100
-8	125	122
-6	261	-259
-4	187	185
-2	82	-79
0	142	145
2	161	-158
4	108	99
H= 10	K= 2	
-15	113	-115
-14	52	50
-13	131	134
-12	69	-66
-11	164	-166
-10	99	108
-9	153	162
-8	92	-92
-7	162	-162
-6	51	42
-5	163	164
-4	67	-63
-3	142	-145
-2	105	103
-1	147	149
0	83	-79
1	142	-136
2	51	47
3	105	97
4	60	-48
H= 10	K= 4	
-13	121	-130
-12	74	-72
-11	109	119
-10	72	69
-9	114	-125
-8	56	-50
-7	152	152
-6	65	67
-5	153	-153
-4	64	-58
-3	130	128
-2	60	51
-1	113	-110
0	59	-69
1	110	107
2	55	48
H= 10	K= 6	
-7	31	-6
-6	107	-108
-5	31	1
-4	94	95
H= 11	K= 1	
-15	121	-123
-14	72	-72
-13	124	130
-12	82	61
-11	128	-140
-10	80	-85
-9	141	149
-8	107	95
-7	141	-147
-6	97	-94
-5	155	146
-4	87	86
-3	138	-137
-2	62	-58
-1	128	129
0	65	59
1	120	-117
2	72	-72
3	100	92
H= 11	K= 3	
-14	110	120
-13	33	2
-12	118	-130
-11	-28	-2
-10	162	178
-9	-26	-13
-8	159	-157
-7	29	15
-6	119	118
-5	33	2
-4	153	-148
-3	-23	5
-2	161	160
-1	28	-8
0	119	-118
1	30	-4
2	96	91
H= 11	K= 5	
-10	45	-40
-9	96	-107
-8	65	67
-7	102	106
-6	87	-86
-5	91	-92
-4	55	51
-3	92	87
-2	53	-44
H= 12	K= 0	
-14	143	-160
-12	151	166
-10	153	-165
-8	190	185
-6	193	-187
-4	163	160
-2	40	-134
0	138	134
2	144	-132
H= 12	K= 2	
-14	68	70
-13	99	105
-12	74	-83
-11	118	-132
-10	90	95
-9	123	128
-8	86	-78
-7	101	-93
-6	82	74
-5	119	119
-4	95	-93
-3	135	-136
-2	95	86
-1	92	87
0	60	-58
1	81	-75
H= 12	K= 4	
-11	96	103
-10	63	62
-9	109	-105
-8	65	-63
-7	109	107
-6	62	53
-5	98	-102
-4	71	-62
-3	90	86
-2	68	58
H= 13	K= 1	
-14	62	-59
-13	128	146
-12	72	81
-11	106	-120
-10	72	-68
-9	142	137
-8	70	62
-7	164	-161
-6	72	-61
-5	132	128
-4	55	57
-3	113	-112
-2	65	-60
-1	120	116
0	60	53
H= 13	K= 3	
-12	94	-106
-11	-28	24
-10	105	111
-9	-27	-14
-8	129	-131
-7	32	-13
-6	119	121
-5	32	-7
-4	106	-105
-3	-26	12
-2	114	103
H= 14	K= 0	
-12	148	157
-10	128	-141
-8	139	132
-6	134	-131
-4	123	123
-2	132	-122
H= 14	K= 2	
-12	44	-48
-11	119	-119
-10	76	73
-9	102	104
-8	86	-84
-7	110	-105
-6	68	62
-5	104	108
-4	59	-54
-3	99	-93
H= 15	K= 1	
-11	101	-107
-10	65	-60
-9	96	100
-8	33	31
-7	102	-100
-6	80	-73
-5	100	98

nitrogens each in a general position set, were clearly indicated. The nitrogen atoms were identified by packing considerations. The model now gave an R value of 0·081, and the structure, including space group choice, was assumed to be generally correct.

A full-matrix least-squares refinement, including anisotropic temperature factors, was made. The quantity minimized was $\Sigma w(F_o - F_c^*)^2$, where w is the weight based on counting statistics (Evans, 1961), and

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

in which K = scale factor, g = extinction correction (Zachariasen, 1963; Larson, 1967), Lp = Lorentz-polarization factor and F_c = the structure factor calculated in the usual way, using the uranium form factors of Cromer & Waber (1965) and the fluorine and nitrogen form factors from *International Tables for X-ray Crystallography* (1962). Dispersion corrections (real part only) were applied to the uranium form factors (Cromer, 1965). The anisotropic temperature factors were in the form

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

The final parameters are given in Table 1. At the end of the refinement all shifts were less than 2×10^{-3} times their standard deviations. Table 2 lists the observed and calculated structure factors which give a final $R = \Sigma|\Delta F|/\Sigma|F_o| = 0{\cdot}048$, with unobserved reflections omitted. Table 3 gives the magnitudes and orientations of the thermal ellipsoids. The large standard deviations of some of the orientation angles in Table 3 arise be-

Table 3. *Thermal ellipsoids in* $(NH_4)_4UF_8$

	Axis i	R.m.s. amplitude	B_i	Angles between ellipsoid axes and monoclinic lattice axes		
				α	β	γ
U	1	0·090 ± 3 Å	0·63 ± 4 Å²	40 ± 2°	90°	161 ± 2°
	2	0·141 ± 2	1·56 ± 4	90	0	90
	3	0·131 ± 2	1·35 ± 4	50 ± 2	90	71 ± 2
F(1)	1	0·192 ± 18	2·90 ± 53	46 ± 13	53 ± 14	92 ± 12
	2	0·246 ± 17	4·79 ± 64	103 ± 11	46 ± 12	118 ± 7
	3	0·115 ± 27	1·04 ± 49	133 ± 12	67 ± 10	29 ± 7
F(2)	1	0·150 ± 22	1·78 ± 53	15 ± 26	93 ± 23	136 ± 32
	2	0·251 ± 17	4·98 ± 66	79 ± 8	35 ± 10	69 ± 9
	3	0·174 ± 18	2·39 ± 51	80 ± 37	125 ± 10	54 ± 34
F(3)	1	0·124 ± 24	1·21 ± 46	29 ± 12	70 ± 15	139 ± 13
	2	0·186 ± 18	2·74 ± 52	100 ± 36	27 ± 51	63 ± 41
	3	0·197 ± 16	3·07 ± 49	63 ± 18	108 ± 69	62 ± 38
F(4)	1	0·173 ± 18	2·36 ± 51	34 ± 16	56 ± 15	115 ± 19
	2	0·231 ± 15	4·22 ± 56	117 ± 13	47 ± 11	105 ± 9
	3	0·126 ± 23	1·25 ± 46	109 ± 18	62 ± 14	30 ± 17
N(1)	1	0·146 ± 30	1·67 ± 70	26 ± 38	88 ± 56	147 ± 42
	2	0·168 ± 27	2·24 ± 73	76 ± 61	37 ± 58	70 ± 60
	3	0·187 ± 25	2·77 ± 75	69 ± 33	127 ± 58	66 ± 36
N(2)	1	0·131 ± 34	1·35 ± 70	42 ± 108	76 ± 129	146 ± 195
	2	0·198 ± 23	3·11 ± 74	124 ± 19	43 ± 19	92 ± 19
	3	0·138 ± 28	1·50 ± 61	69 ± 158	51 ± 64	67 ± 196

Table 4. *Interatomic distances and bond angles*

U–F(1) = 2·28 ± 0·01 Å
F(2) = 2·27
F(3) = 2·33
F(4) = 2·25

F(1)–F(2) = 2·63 ± 0·02
F(1)–F(2′) = 2·84
F(1)–F(3) = 2·77
F(1)–F(4) = 2·90
F(2)–F(3) = 2·78
F(2)–F(4) = 3·17
F(3)–F(4) = 2·74
F(3)–F(4′) = 2·67

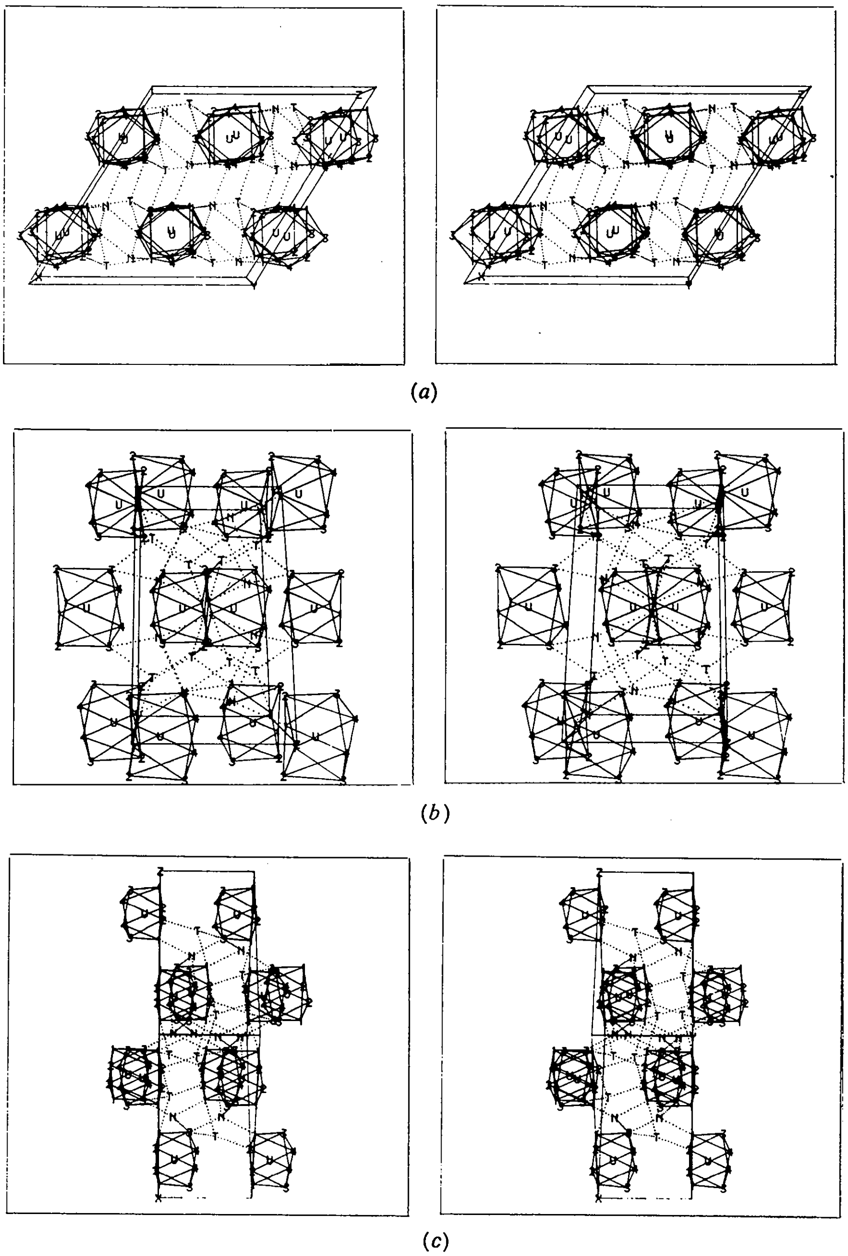
N(1)–F(1) = 2·70 ± 0·02 Å
–F(3) = 2·82
–F(3′) = 2·77
–F(4) = 2·75

N(2)–F(1) = 2·81 ± 0·02 Å
–F(2) = 2·85
–F(2′) = 2·79
–F(3) = 2·77
F(1) –N(1)–F(3) = 126 ± 0·5°
F(1) –N(1)–F(3′) = 87
F(1) –N(1)–F(4) = 108
F(3) –N(1)–F(3′) = 95
F(3) –N(1)–F(4) = 122
F(3′)–N(1)–F(4) = 109
F(1) –N(2)–F(2) = 113 ± 0·5°
F(1) –N(2)–F(2′) = 128
F(1) –N(2)–F(3) = 85
F(2) –N(2)–F(2′) = 104
F(2) –N(2)–F(3) = 117
F(2′)–N(2)–F(3) = 110

cause the magnitudes of two ellipsoid axes are nearly the same. No anomalies suggesting that the space group has been chosen incorrectly are observed in these thermal parameters. The thermal parameters support the assignment of fluorine and nitrogen atoms.

Discussion

Three stereo-pair views of the structure are shown in Fig. 2. Fig. 3 is a projection of the structure on the *ac* plane. Each uranium atom lies at the center of an isolated polyhedron of eight fluorine atoms at distances ranging from 2·25 to 2·33 Å, the average being 2·28 Å. The polyhedron of fluorine atoms, shown with thermal ellipsoids in Fig. 4, is drawn as, and may be regarded as, a distorted tetragonal antiprism. If a line is drawn to join the two F(2) atoms and another to join the two F(4) atoms, it can be seen that the polyhedron can also be regarded as a distorted trigonal dodecahedron. The anti-prism configuration, somewhat less distorted, but


(*a*)

(*b*)

(*c*)

Fig. 2. Stereo views of the $(NH_4)_4UF_8$ structure along (*a*) *b* axis, (*b*) *c* axis, (*c*) [101] zone axis. *X*, *Y*, *Z* define unit lengths of the cell edges *a*, *b*, *c* and thus define the origin. N and T represent N(1) and N(2) respectively. The non-equivalent fluorines are numbered 1 through 6.

with shared corners, has been described for several compounds, for example UF_4 (Larson, Roof & Cromer 1964) and $(NH_4)_2CeF_6$ (Ryan, Kruse & Larson, 1967), and the tetragonal dodecahedron configuration has been described in Rb_2UF_6 (Kruse, 1967). The configuration in this structure may thus be regarded as intermediate between these two types. In the structure of Li_4UF_8 (Brunton, 1967), the uranium atom has eight near fluorine neighbors at the approximate distances found in the present structure, plus a ninth fluorine atom at the considerably greater distance of 3·30 Å. This configuration may be thought of as a tetragonal antiprism in which the atoms of the base of the prism have moved apart to allow the approach of the ninth atom. In $LiUF_5$ (Brunton, 1966) this ninth fluorine atom of the polyhedron moves still closer (2·59 Å). The final result of this transition from eight- to nine-coordination is the configuration in K_2PaF_7 (Brown & Smith, 1965) where the nine fluorine neighbors form a trigonal prism with an atom opposite each face and in the equatorial plane of the prism. The average length of the equatorial Pa–F bonds is 2·38 Å, and that of the prism Pa–F bonds is 2·21 Å. The shortest interpolyhedron F–F bond in $(NH_4)_4UF_8$ is 2·92 Å.

N(1) has four fluorine neighbors at distances of 2·70 to 2·82 Å and four additional fluorine neighbors at 2·99 to 3·81 Å. N(2) has four fluorine neighbors at distances of 2·77 to 2·85 Å and three additional ones at 2·98 to 3·08 Å. The four nearest neighbors are rather roughly tetrahedrally disposed, suggesting that these distances represent N–H---F hydrogen bonds.

Pertinent interatomic distances and bond angles are listed in Table 4.

The nature of the perfect (001) cleavage is clearly seen in Fig. 2(*a*). The U–F coordination polyhedra are arranged in layers parallel to (001), and these layers are

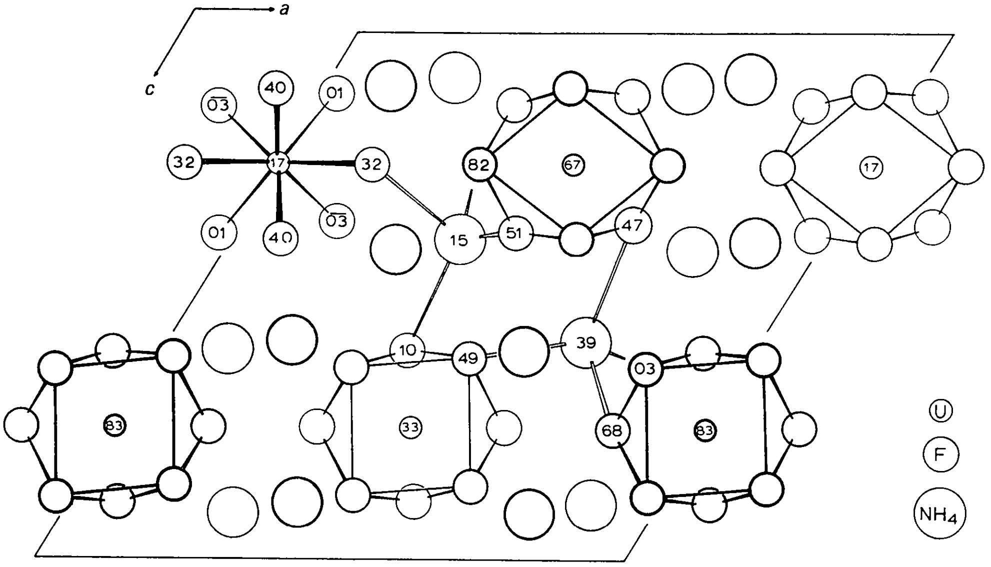


Fig. 3. Projection of the structure of $(NH_4)_4UF_8$ on the *ac* plane. Numbers indicate the *y* coordinate of the atoms in hundredths of *b*. For the uranium at 0·17 the U–F bonds are shown, for others the outline of the fluorine polyhedron is shown.

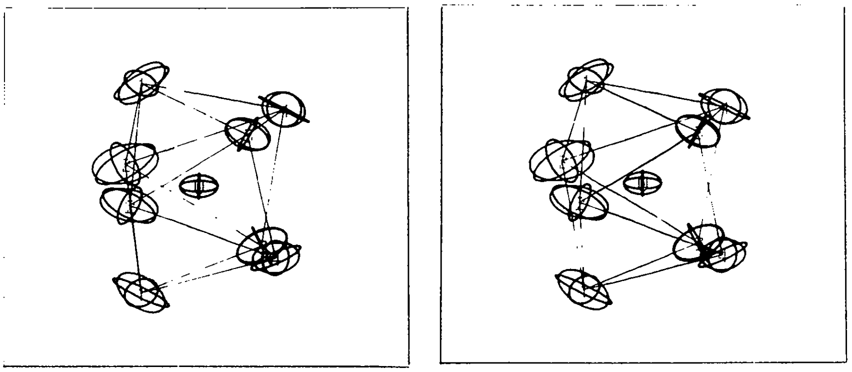


Fig. 4. Stereo-pair of the U–F coordination and thermal ellipsoid viewed along the a^* axis, with the *b* axis horizontal.

joined to one another by a series of nearly parallel N–F bonds at heights of $z=0.\frac{1}{2}$. The prominent (001) face is also explained by this layer structure. The remaining prominent morphological forms are also related to layer arrangements, though less distinctive, of the coordination groups along other directions. These are seen in Fig. 2(*a*) parallel to (100), in the *c* axis view [Fig. 2(*b*)] parallel to (110), and in the [101] zone-axis view [Fig. 2(*c*)] parallel to $(11\bar{1})$.

The persistent simple twinning on (001) suggests that the structure is such that reflection across a plane parallel to (001) results in a twin boundary configuration common to the two individuals with only slight distortion in the relative position of near neighbors. A configuration across the twin boundary identical to that of the single crystal is not to be expected, for in that case the twinning would likely be polysynthetic, and this has not been observed. Three possible twinning operations can be considered: (1) reflection at $z=\frac{1}{4}$, (2) reflection at $z=0$ and (3) glide reflection at $z0$ with a translation of $a/2$. The first case results in a distortion of the U–F coordination, the second and third cases result in a distortion of the N–F coordination. In case (1) two F–F bonds of 2·84 Å within the polyhedron change to 2·53 and 3·13 Å. In case (2) the N–F bonds across the cleavage plane change from 2·75 and 2·85 Å to 3·17 and 2·44 Å, respectively. The average bond angle for N(1) increases to 116° but does not change significantly for N(2). In case (3) the N–F bonds across the cleavage plane change from 2·75 and 2·85 Å to 2·59 and 2·49 Å, respectively, with no significant change in the average bond angles. It is difficult to make a valid choice between these possibilities although case (2) appears least likely because of the great increase in the N(1)–F bond. Case (1) appears most likely since, if a distortion of the polyhedron is permitted at all, the short F–F bond (2·53 Å) could be lengthened and the corresponding N–F bonds adjusted slightly while still retaining all the bond lengths within the range that exists in the single crystal structure.

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Die Kristallstruktur von Triisopropylidencyclopropan

Von Hans Dietrich

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem, Deutschland

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The crystal structure of triisopropylidenecyclopropane has been determined from X-ray diffraction data. The space group is $P6_1$ and the cell data are $a=9{\cdot}39$; $c=21{\cdot}36$ Å; $V=1631$ Å^3; $n=6$. The flat molecules are arranged in sheets perpendicular to the hexagonal axis. The bond lengths within the cyclopropane ring are shortened (1·451 Å) because of the three adjacent double bonds, whereas the double bonds (1·333 Å) are of normal length. The crystalline substance is sensitive to X-rays.

Die Molekülstruktur des von Köbrich und Mitarbeitern (Köbrich & Heinemann, 1965; Köbrich, Heinemann & Zündorf, 1967) synthetisierten Triisopropylidencyclopropans ist von Interesse wegen der unmittelbaren Nachbarschaft von drei an Doppelbindungen beteiligten Kohlenstoffatomen. Die Wechselwirkung der π-Elektronen im Triisopropylidencyclopropan und ähnlichen gekreuzt konjugierten Systemen war daher auch schon Gegenstand quantenchemischer Berechnungen (Weltin, Gerson, Murrell & Heilbronner, 1961; Heilbronner, 1966).

Elementarzelle und Raumgruppe ($P6_1$, C_6^2) der Substanz waren schon früher von Dunitz & Mugnoli (1966) bestimmt worden. Die Zellparameter konnten