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The Crystal Structure of Uranium Pentachloride

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UCl_5 forms monoclinic crystals with lattice constants: $a=7{\cdot}99$, $b=10{\cdot}69$, $c=8{\cdot}48$ Å; $\beta=91{\cdot}5°$. The space group is $P2_1/n$, and the unit cell contains four UCl_5 units. Full-matrix least-squares refinement of diffractometrically measured X-ray diffraction data resulted in a final R of 6·0%.

The structure is based on a cubic closest packing of chlorine atoms, in which uranium atoms occupy one-fifth of the octahedral holes. Two such octahedra share an edge to form a dimeric U_2Cl_{10} unit. U-Cl distances involving bridging Cl are 2·67 and 2·70 Å; those involving non-bridging chlorine atoms are 2·43, 2·43, 2·44, and 2·44 Å. Uranium atoms in the U_2Cl_{10} units are each shifted by about 0·20 Å from the centers of the octahedra in directions away from one another. The relation of the structure of UCl_5 to those of $NbCl_5$ and α-UF_5 is discussed.

Introduction

In the uranium-chlorine system, four compounds are known (Katz & Rabinowitch, 1961): UCl_3, UCl_4, UCl_5, and UCl_6. Of these, the pentachloride is probably the least studied, because of manipulative difficulties. (In addition to being moisture-sensitive, UCl_5 can disproportionate into UCl_4 and UCl_6 and/or can thermally decompose to UCl_4.) The crystal structure of UCl_5 has not been reported previously, although Zachariasen (1948) mentioned that the crystals are monoclinic. Recent work in this Laboratory (Dodge, Smith, Johnson & Elson, 1966) showed that the pentachloride of the neighboring actinide element, protactinium, forms monoclinic crystals with a molecular structure unlike any previously known halide. It was therefore of interest to see whether or not uranium pentachloride is isostructural. The present structure determination shows, instead, a different crystalline arrangement for UCl_5.

Experimental

Crystals of UCl_5 were obtained by the following procedure: about 10 mg of U_3O_8 was placed in one end of a quartz tube, after which a medium-porosity fritted disc was sealed about ½ inch from the end. The assembly was connected to a vacuum line, and the oxide treated with gaseous carbon tetrachloride at ~400°C to produce what was probably a mixture of UCl_4, UCl_5, and their oxychlorides. Enough carbon tetrachloride was then distilled into the tube to fill about half the volume below the frit, the tube sealed off (about 1 inch above the frit), and heating continued overnight at ~225°C. After cooling to ~100°C, all solids and the dark brown solution were placed on one side of the frit, and the other section was washed by distilling carbon tetrachloride vapor into it. The tube was inverted, and the saturated solution of UCl_5 in carbon tetrachloride was filtered through the frit (UCl_3, UCl_4, *etc.* are insoluble in carbon tetrachloride.) The solution was then slowly cooled to room temperature over a period of 2 hours, resulting in the formation of a number of large crystals. The tube was again inverted and slowly centrifuged, and the crystals washed by distilling carbon tetrachloride over them. Finally, the tube was opened in a dry-box, and a half-dozen or so of the dark brown crystals were sealed in thin-walled glass capillaries for X-ray examination. Only minute amounts of the green tetrachloride were seen.

Single-crystal diffraction photographs showed monoclinic symmetry; the systematic extinctions ($h0l$, $h+l=2n+1$; $0k0$, $k=2n+1$) are those uniquely characterizing the space group $P2_1/n$. Unit-cell data are as follows (Mo $K\alpha=0{\cdot}7107$ Å): $a=7{\cdot}99$, $b=10{\cdot}69$, $c=8{\cdot}48$ Å; $\beta=91{\cdot}5°$ (with an accuracy of about 0·3%); the calculated density, 3·81 g.cm^{-3}, for four UCl_5 units per unit cell concurs with the experimental value of 3·81 g.cm^{-3} (Katz & Rabinowitch, 1961).

Intensity measurements were carried out on a General Electric XRD-5 diffractometer equipped with a goniostat. The crystal specimen was a prism (along the a axis) measuring about 0·40 mm in length and 0·23 × 0·16 mm in cross section. Although this crystal was somewhat larger than desired, glove-box manipulations of smaller crystals proved to be quite difficult. The stationary-crystal stationary-counter technique (Furnas, 1957) was used; the radiation was Zr-filtered Mo $K\alpha$. In all, 495 reflections were recorded up to a 2θ-cutoff of 36°. Reflections at $\chi=90°$ showed an intensity variation with φ of about ±40% (the linear absorption coefficient for Mo $K\alpha$ radiation is ~290 cm^{-1}). These measurements were used to obtain φ-dependent absorption corrections which were applied to all reflections. The corrected intensities were reduced to relative $|F|$'s through the application of Lorentz–polarization factors.

Determination of the structure

A three-dimensional Patterson synthesis was readily interpreted to give the location of the uranium atoms. Chlorine atoms in octahedral coordination about uranium could also be recognized; their positions, however, were located from a 'heavy-atom' electron-density synthesis. All atoms were found to occupy fourfold general positions in $P2_1/n\,[\pm(x,y,z);\ \pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)]$. Thus, with individual isotropic temperature factors there are 25 parameters to be determined from the 495 measured reflections.

The structure model was refined by the full-matrix least-squares program of Gantzel, Sparks & Trueblood (ACA Program No. 317, unpublished). The atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962) for the neutral atoms. The refinement was based on $|F|$ with the following weighting scheme (Smith, Johnson & Nordine, 1965): $w=F_o^{1/4}$, $F_o<A$; $w=A^{5/4}F_o^{-1}$, $F_o>A$. When the structure factors were placed on an absolute scale, A was 154. Five cycles of refinement reduced the conventional R value to 6·0% (all reflections). Changes in the parameters at this point were $\leq 0{\cdot}010$ times the standard deviations.

A final difference map showed no disquieting features; the largest peak height amounted to only 1·2 e.Å^{-3}. This peak, about 1 Å distant from the uranium atom, is part of some rather broad detail, apparently due to absorption effects. For purposes of further comparison, a refinement series was carried out on $|F|$'s which were uncorrected for absorption. The R value for this refinement was 12·6%; parameters, however, in all cases save one were within 2σ of the values obtained when the absorption factors were applied. These results indicate the effectiveness of the absorption corrections in providing a substantially better fit between observed and calculated data.

Parameters from the $R=6{\cdot}0\%$ refinement were accepted as final, and are given in Table 1. Table 2 lists observed and calculated structure factors.

Table 1. *Final parameters in* UCl_5

All atoms in general positions, e.s.d.'s in parentheses.

Atom	10^4x	10^4y	10^4z	B
U	−523 (2)	1378 (1)	1653 (2)	2·9 ± 0·1 Å^2
Cl(1)	389 (13)	1111 (9)	−1374 (12)	2·6 ± 0·2
Cl(2)	−1388 (14)	1275 (12)	4384 (13)	3·6 ± 0·3
Cl(3)	2443 (15)	1267 (12)	2409 (14)	3·6 ± 0·3
Cl(4)	−3414 (14)	1265 (11)	693 (13)	3·4 ± 0·3
Cl(5)	−464 (14)	3657 (11)	1469 (13)	3·5 ± 0·3

Discussion of the structure

Each uranium atom is coordinated octahedrally to six chlorine atoms; two such octahedra share an edge to form a U_2Cl_{10} unit (Fig. 1) which is situated at a crystallographic center of inversion. (There are two dimers per unit cell.) This dimeric configuration is very similar to those found in the solid state for $NbCl_5$ and $TaCl_5$ (Zalkin & Sands, 1958) and $MoCl_5$ (Sands & Zalkin, 1959). At the same time, the configuration differs totally

Table 2. *Observed and calculated structure factors*

```
H,K= 0, 0
L FOB FCA
 2 164-162
 4 176-171
 6 162 152

H,K= 0, 1
L FOB FCA
 1 133 123
 2 229-226
 3 207-198
 4 175 174
 5  59  58
 6   1   2
 7  59  50

H,K= 0, 2
L FOB FCA
 0  61 -55
 1 309-297
 2  29  23
 3   1  -7
 4  18  17
 5  44  57
 6  24 -26
 7 116-112

H,K= 0, 3
L FOB FCA
 1 131-126
 2 122-121
 3 242 218
 4 100 105
 5  66 -75
 6   1  -7

H,K= 0, 4
L FOB FCA
 0 474-491
 1  83  83
 2 126 123
 3   7   7
 4 160 133
 5  56 -51
 6 130-123

H,K= 0, 5
L FOB FCA
 1  59 -62
 2 216 211
 3 100  98
 4 186-164
 5  33 -22
 6  14  -9

H,K= 0, 6
L FOB FCA
 0  94 105
 1 155 178
 2  47 -46
 3  10   6
 4  44 -36
 5  44 -37

H,K= 0, 7
L FOB FCA
 1  80  85
 2  12  22
 3 160-156
 4  30 -27

H,K= 0, 8
L FOB FCA
 0 242 231
 1  89 -93
 2  65 -62
 3  10  -8

H,K= 0, 9
L FOB FCA
 1  17  16

H,K= 1, 0
L FCB FCA
-7  64  69
-5 140 157
-3 461-491
-1  77  74
 1 273 273
 3 234-240
 5  31  31
 7 189 190

H,K= 1, 1
L FCB FCA
-7 119 117
-6 114 116
-5 104-117
-4  38 -49
-3  62 -67
-2 142-145
-1 282 262
 0 255 226
 1 188-174
 2  31 -30
 3  70 -72
 4 119-118
 5 145 147
 6  97  95
 7  69 -71

H,K= 1, 2
L FOB FCA
-7   1  -4
-6  49  51
-5  16 -25
-4 240-260
-3  41  42
-2 165 172
-1  13  -7
 0 121 110
 1  41 -34
 2  42 -48
 3  35  37
 4 134 139
 5   1  -7
 6  25  30
 7  20 -17

H,K= 1, 3
L FOB FCA
-6 126-133
-5  55 -65
-4  38  44
-3  48 -45
-2 156 165
-1 145 141
 0 237-238
 1  98 -93
 2  38  39
 3  32 -33
 4 133 131
 5  76  81
 6 113-116

H,K= 1, 4
L FCB FCA
-6   1  -8
-5 127-126
-4  72  68
-3 362 367
-2  61 -62
-1  55 -54
 0  27 -31
 1 201-202
 2  79  79
 3 193 188
 4  40 -41
 5  29 -26
 6  22 -21

H,K= 1, 5
L FOB FCA
-6  68 -60
-5 131 119
-4  22  33
-3  53  58
-2  67  68
-1 231-240
 0 105-109
 1 157 160
 2  11  11
 3  77  75
 4  73  61
 5 171-150
 6  51 -44

H,K= 1, 6
L FOB FCA
-5  54  53
-4 161 168
-3  84 -85
-2  93-110
-1  23  15
 0  68 -66
 1  70  69
 2  49  53
 3  76 -76
 4 103 -90
 5  18  16

H,K= 1, 7
L FOB FCA
-4  23 -27
-3  19  16
-2 110-120
-1  24 -27
 0 151 163
 1  19  17
 2  29 -30
 3  18  -0
 4 102 -95

H,K= 1, 8
L FOB FCA
-3 177-190
-2  66  70
-1  30  26
 0  60  35
 1 102  99
 2  92 -92
 3 105 -96

H,K= 1, 9
L FOR FCA
-1 139 152
 0  28  24
 1 104-100

H,K= 2, 0
L FOB FCA
-6 222 232
-4  24  17
-2 236-242
 0 280 264
 2  41  37
 4 343-367
 6 133 134

H,K= 2, 1
L FOB FCA
-7   1   3
-6  72  76
-5 100 108
-4 167-179
-3 143-142
-2  83  82
-1  33 -25
 0 169 154
 1 188 178
 2 207-205
 3 127-126
 4  64  66
 5  27 -29
 6  87  90

H,K= 2, 2
L FOB FCA
-6  18 -22
-5  36 -47
-4   1  -7
-3 148-150
-2  39  38
-1  63  50
 0  39 -34
 1 110-100
 2   6  -5
 3 127-133
 4  33  33
 5 200 204
 6  17 -20

H,K= 2, 3
L FGB FCA
-6  60  52
-5 134-132
-4  98-103
-3 163 156
-2  36  36
-1  39  33
 0  83  84
 1 209-197
 2 116-109
 3 150 145
 4  42  44
 5  22  26
 6  44  51

H,K= 2, 4
L FUB FCA
-6 194-190
-5  33  27
-4  18 -15
-3  30  40
-2 184 189
-1  78 -79
 0 198-199
 1  32  33
 2  34 -28
 3  51  49
 4 329 289
 5  61 -56
 6 107-110

H,K= 2, 5
L FOR FCA
-5  52 -49
-4 186 176
-3  75  74
-2  85 -86
-1  13   9
 0 134-143
 1  88 -87
 2 204 203
 3  63  61
 4  69 -60
 5  17  21

H,K= 2, 6
L FCH FCA
-5  28  32
-4   1  14
-3  96  96
-2  75 -78
-1  49 -54
 0  67  68
 1  61  63
 2  18  10
 3  85  87
 4  71 -69
 5 166-137

H,K= 2, 7
L FOB FCA
-4  19  22
-3 109-111
-2  11   1
-1  24 -25
 0  19 -16
 1 138 141
 2  16  16
 3 108-108
 4  21 -16

H,K= 2, 8
L FOB FCA
-3  43 -47
-2 100 -96
-1  89  92
 0 100  99
 1  37 -38
 2  19  14
 3  58 -58

H,K= 3, 0
L FOB FCA
-5 144 153
-3 164-169
-1 113-114
 1 464 489
 3 130-137
 5 101-114

H,K= 3, 1
L FOB FCA
-6  67  60
-5   7  -6
-4  50  53
-3 149-158
-2 160-162
-1 178 183
 0 117 108
 1  13 -16
 2  82  80
 3 166-166
 4 153-153
 5 123 128
 6  45  44

H,K= 3, 2
L FOB FCA
-6 117 119
-5  21 -27
-4  54 -61
-3  16  18
-2   1  11
-1  18  19
 0 241 230
 1  50 -42
 2 246-224
 3  14  18
 4   1   1
 5   5  11
 6  45  45

H,K= 3, 3
L FOB FCA
-6  75 -66
-5   1   6
-4  67 -70
-3 101 -96
-2 180 186
-1  95  97
 0 120-115
 1   7 -10
 2  93 -87
 3 103 -96
 4 174 171
 5  74  78
 6  57 -57

H,K= 3, 4
L FOB FCA
-5 134-123
-4  60  51
-3 132 133
-2   9 -11
-1  89  89
 0  68 -66
 1 360-369
 2  71  67
 3 115 109
 4  10   1
 5  90  93

H,K= 3, 5
L FOB FCA
-5  16  15
-4  20 -20
-3 142 149
-2  75  79
-1 176-182
 0  51 -58
 1  22  15
 2  44 -42
 3 168 163
 4  91  82
 5 143-126

H,K= 3, 6
L FOB FCA
-4  39  39
-3  43 -38
-2   1  -9
-1  39 -39
 0 138-146
 1  90  86
 2 145 145
 3  38 -38
 4   5   0

H,K= 3, 7
L FOB FCA
-3  30  26
-2 131-137
-1  15 -14
 0  79  81
 1   9   3
 2  63  63
 3  21  21

H,K= 3, 8
L FOB FCA
-2  17  13
-1  47 -46
 0  73  78
 1 198 192

H,K= 4, 0
L FOB FCA
-6  68  70
-4 122 125
-2 382-371
 0  77  74
 2 161 173
 4 151-166

H,K= 4, 1
L FOB FCA
-6 111 108
-5 101  99
-4  96-103
-3  40 -50
-2  40 -41
-1 104-105
 0 205 195
 1 167 167
 2 113-120
 3  24 -25
 4  36 -42
 5  68 -70

H,K= 4, 2
L FOB FCA
-5  39  43
-4  17 -21
-3 215-217
-2  33  34
-1 142 144
 0  12  -7
 1  75  71
 2  21 -23
 3  64 -69
 4  23  25
 5  87  91

H,K= 4, 3
L FOB FCA
-5 121-117
-4  47 -56
-3  48  48
-2  32 -29
-1 120 124
 0 118 114
 1 185-184
 2  69 -68
 3  31  31
 4  13 -21
 5  57  79

H,K= 4, 4
L FOB FCA
-5   1  -5
-4 113-102
-3  58  56
-2 294 293
-1  53 -51
 0  62 -58
 1  16 -18
 2 137-137
 3  60  54
 4 146 134
 5  28 -29

H,K= 4, 5
L FCB FCA
-4 120 107
-3  22  34
-2  37  36
-1  53  51
 0 196-188
 1  82 -88
 2 122 120
 3  11  10
 4  45  45

H,K= 4, 6
L FOB FCA
-3 142 144
-2  74 -72
-1  92 -95
 0  23  15
 1  46 -46
 2  53  48
 3  49  45

H,K= 4, 7
L FOB FCA
-2  21  12
-1  92 -94
 0  27 -27
 1 135 133
 2  12  13

H,K= 5, 0
L FOB FCA
-5 203 196
-3  12  -2
-1 164-167
 1 151 170
 3   8  11

H,K= 5, 1
L FOB FCA
-5  57  57
-4  85  86
-3 145-147
-2 111-114
-1  53  62
 0  18 -12
 1  81  89
 2  93 100
 3 113-116
 4  78 -79

H,K= 5, 2
L FOB FCA
-4  52 -48
-3   1  -4
-2 109-108
-1  25  26
 0  69  73
 1  23 -23
 2  61 -63
 3   1  -2
 4  76 -72

H,K= 5, 3
L FOB FCA
-4 107-106
-3  91 -89
-2 126 127
-1  24  29
 0  17  17
 1  48  52
 2 121-117
 3  72 -61
 4  95  92

H,K= 5, 4
L FOB FCA
-4  26  24
-3   1   1
-2  25  27
-1 130 134
 0  62 -55
 1 129-137
 2  23  24
 3   5  -8

H,K= 5, 5
L FOB FCA
-3 144 145
-2  58  62
-1  65 -68
 0  17   4
 1  78 -88
 2  52 -50
 3 125 122

H,K= 5, 6
L FOB FCA
-2  74  72
-1  55 -56
 0  59 -47
 1  48  48

H,K= 6, 0
L FOB FCA
-2 107-116
 0  62 -57
 2 240 245

H,K= 6, 1
L FOB FCA
-3  17  34
-2  92 -99
-1  89 -95
 0 111 106
 1  66  68
 2  11 -17
 3  41  39

H,K= 6, 2
L FOB FCA
-3  53 -53
-2   1  13
-1   1   9
 0  14  11
 1 139 126
 2  24 -24
 3 135-125

H,K= 6, 3
L FOB FCA
-3  46 -46
-2  57 -62
-1 113 113
 0  62  56
 1  76 -75
 2   9 -10

H,K= 6, 4
L FOB FCA
-2  88  94
-1  12 -10
 0  51  46
 1  38 -38
```

from the infinite chains of pentagonal bipyramids sharing edges found in protactinium pentachloride (Dodge, Smith, Johnson & Elson, 1967).

The U–Cl bond lengths to non-bridging Cl are 2·43, 2·43, 2·44, and 2·44 Å (Table 3), all with standard deviations of 0·01 Å. These agree excellently with the U–Cl bond distance of 2·42 ± 0·1 Å reported for the octahedral molecule, UCl$_6$ (Zachariasen, 1948). U–Cl bond lengths to the bridging chlorines, Cl(1) and Cl(1′), are significantly longer at 2·70 and 2·67 Å, respectively. Similar variations between bonds to bridging and non-bridging Cl are known in a number of complexes, including, for example, NbCl$_5$ and MoCl$_5$. Interestingly enough, the U–Cl bond distances involving both bridging and non-bridging chlorines are very similar to those found in PaCl$_5$, despite the fact that Pa is seven- rather than six-coordinate.

The uranium atoms are each shifted by about 0·20 Å from the centers of the octahedra in directions *away* from one another, *i.e.* along the line joining U and U′ (Fig. 1). The bridging chlorine atoms Cl(1) and Cl(1′), partially collapse toward one another so that their interatomic distance of 3·39 Å is shorter than the intra-octahedron Cl···Cl contacts (3·53 – 3·64 Å) not involving either Cl(1) or Cl(1′). As a result of these two distortions, bond angles within the octahedra deviate noticeably from 90°. In particular, the Cl(1)–U–Cl(1′) angle is compressed to 78·4°.

The crystal structure as a whole is based on the cubic closest packing (c.c.p.) of Cl atoms, in which uranium atoms occupy one-fifth of the octahedral holes. This arrangement is illustrated in Fig. 2, where the square nets (in the present case, quasi-square nets) characteristic of c.c.p. are shown. Overlay of successive nets gives rise to the formation of sub-cellular, face-centered cubes of Cl atoms. For the present arrangement of uranium atoms and for the idealized case of exact c.c.p. of chlorine, simple geometrical considerations require that the repeat distance along the b axis be $4\sqrt{2}$ times R (R = the packing radius of Cl). Similarly, the a- and c-axis repeat distances should both be equal to $2\sqrt{5}\,R$. Numerical values obtained for $R = 1{\cdot}80$ Å (Pauling, 1960) are: $a = c = 8{\cdot}05$ Å, $b = 10{\cdot}18$ Å, compared with experimental values of $a = 7{\cdot}99$, $b = 10{\cdot}69$, $c = 8{\cdot}48$ Å. The observed monoclinic angle of 91·5° deviates slightly from 90°. These calculated lattice parameters are expected to represent minimum values, since the effect of introducing uranium atoms into the octahedral holes should, if anything, cause an expansion of the Cl lattice.

It should also be pointed out that the c.c.p. of Cl in UCl$_5$ is in contradistinction to the case for NbCl$_5$, TaCl$_5$, and MoCl$_5$, where the Cl are in hexagonal closest packing (h.c.p.). Thus, UCl$_5$ and NbCl$_5$ repre-

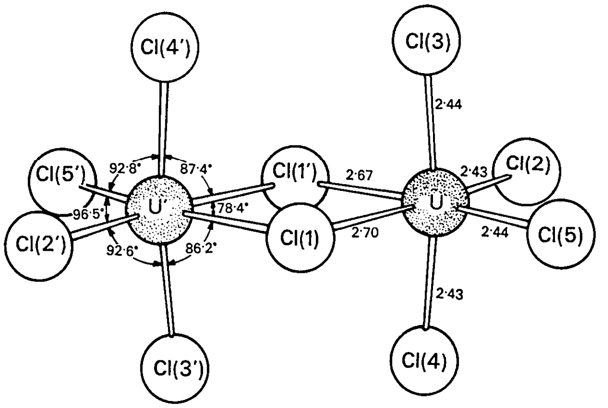

Fig. 1. Configuration of U$_2$Cl$_{10}$ dimer. Distances in Å. A primed atom is related to its corresponding unprimed atom by a center of inversion.

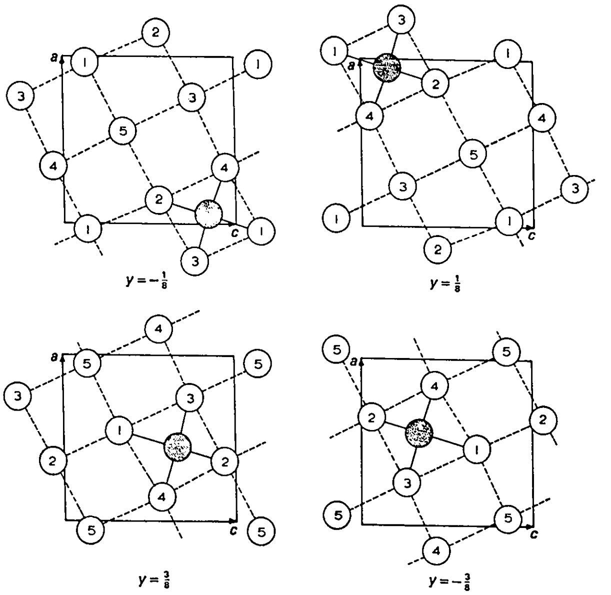

Fig. 2. Sequence of networks along the b axis. Chlorine positions are based on a cubic closest packing arrangement; uranium atoms occupy octahedral sites. The various chlorine atoms are indicated by numbers, uranium atoms by stippling.

Table 3. *Distances and angles in* UCl$_5$*

U —Cl(1)	2·700 ± 0·010 Å	Cl(1)–U–Cl(5)	92·2 ± 0·4°
U —Cl(1′)	2·674 ± 0·010	Cl(2)–U–Cl(1′)	93·0 ± 0·4
U —Cl(2)	2·434 ± 0·011	Cl(2)–U–Cl(3)	92·6 ± 0·4
U —Cl(3)	2·443 ± 0·012	Cl(2)–U–Cl(4)	91·5 ± 0·4
U —Cl(4)	2·432 ± 0·011	Cl(2)–U–Cl(5)	96·5 ± 0·4
U —Cl(5)	2·442 ± 0·012	Cl(3)–U–Cl(1′)	86·2 ± 0·4
U —U′	4·165 ± 0·003	Cl(3)–U–Cl(5)	92·6 ± 0·4
Cl(1)–U–Cl(1′)	78·4 ± 0·3°	Cl(4)–U–Cl(1′)	87·8 ± 0·4
Cl(1)–U–Cl(3)	87·8 ± 0·4	Cl(4)–U–Cl(5)	92·8 ± 0·4
Cl(1)–U–Cl(4)	87·4 ± 0·3	U–Cl(1)–U′	101·6 ± 0·3

* Numbering of atoms follows that of Fig. 1. e.s.d.'s include only uncertainties in the positional parameters.

sent two crystallographically distinct ways of forming M_2Cl_{10} dimeric units within the solid state. Polymorphic transformations between the c.c.p. and h.c.p. arrays would appear very likely. The Cl arrangement in crystalline $PaCl_5$ does not follow either of these two packing modes. Rather, the infinite chains are themselves arranged in a quasi-hexagonal bundle.

In the c.c.p. arangement, each Cl has 12 Cl neighbors at the vertices of a cuboctahedron. Because of the distortions within the chlorine framework, the cuboctahedral coordination about each Cl is not, in general, regular. When sorted out, contacts between Cl in the same octahedron about U show the tendency to be shorter than those between Cl in different octahedra. The ranges of values are 3·39–3·71 Å and 3·65–3·95 Å, respectively (Table 4). In addition to having 12 Cl neighbors, Cl(2), Cl(3), Cl(4), and Cl(5) are each bonded to one uranium; Cl(1) is the exception in being bonded to two uranium atoms. Fig. 3 shows a typical coordination polyhedron; the others may be found by overlaying the networks of Fig. 2.

The present structure is closely related to that of α-UF_5 (Zachariasen, 1949). α-UF_5 is tetragonal with $a=6\cdot529$, $c=4\cdot472$ Å; $c/a=0\cdot685$. The fluorine atoms are in (quasi-) c.c.p. with square nets of the type in Fig. 3 occurring along the c axis. Uranium atoms again occupy one-fifth of the octahedral holes, but with the difference that the octahedra share *vertices* to form infinite chains parallel to **c**. Thus, the repeat distance along the stacking direction occurs after two layers in α-UF_5, rather than four layers in UCl_5. For exact c.c.p. of F, predicted values of the lattice parameters in α-UF_5 become $a=2\sqrt{5}\,R_F$ and $c=2\sqrt{2}\,R_F$ (R_F = packing radius of F); $c/a=0\cdot632$. Numerical values for $R_F=1\cdot35$ Å (Pauling, 1960) are $a=6\cdot04$, $c=3\cdot82$ Å. As expected, the predicted values are too small, uranium atoms evidently causing an expansion of the fluorine framework. In particular, elongation of the octahedra through the agency of bridging fluorines appreciably lengthens the observed c-axis repeat distance.

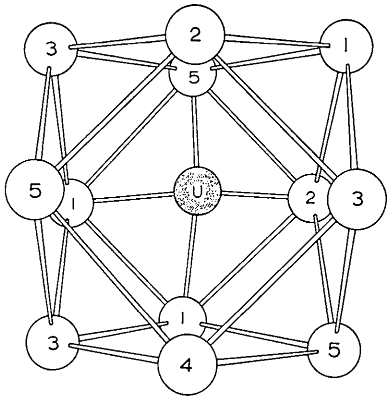

Fig. 3. Coordination polyhedron about Cl(4). This central atom is omitted for the sake of clarity. The twelve chlorine neighbors are at the vertices of a cuboctahedron. View is normal to the y direction of a right-handed coordinate system. Values of y increase from bottom to top of page; values of z increase going to right, but z axis is tipped 20° into page (*cf.* Fig. 2).

Table 4. *Nearest neighbor* Cl(i)–Cl(j) *distances in* UCl_5

Distances (Å) given only for $j\geq i$. Asterisks denote distances within same octahedron.

i j	*d*	*i j*	*d*	*i j*	*d*
1−1	3·39*	2−5	3·83	3−4	3·65
−2	3·71*	−2	3·65	−4	3·87
−2	3·84	−3	3·53*	−4	3·91
−2	3·84	−3	3·80	−5	3·53*
−3	3·50*	−3	3·95	−5	3·79
−3	3·57*	−4	3·48*	−5	3·79
−3	3·79	−4	3·70	4−4	3·87
−4	3·54*	−5	3·64*	−5	3·53*
−4	3·55*	−5	3·75	−5	3·80
−4	3·88	−5	3·82	−5	3·90
−5	3·71*			5−5	3·85

Standard deviation in the d's = 0·02 Å.

The description of the structure in terms of a closest-packed array leaves open the question whether the U_2Cl_{10} dimers have an independent existence as discrete molecules. For example, are the U_2Cl_{10} dimers retained upon solution of UCl_5 in an inert solvent or upon a change of state? The only information bearing on this subject that we are aware of is the molecular-weight study (Katz & Rabinowitch, 1961) which indicates the presence of U_2Cl_{10} dimers in CCl_4 solutions. On the other hand, $NbCl_5$ has a trigonal bipyramidal configuration in the vapor phase, and while the evidence concerning its molecular configuration in solution is not as convincing, the spectroscopic results of Carlson (1963) also favor the monomeric, trigonal bipyramidal arrangement. This apparent difference of behavior in solution is a further point of dissimilarity between UCl_5 and $NbCl_5$.

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