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UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

# The Crystal Structure of Thorium Tetraiodide[1]

BY ALLAN ZALKIN, J. D. FORRESTER, AND DAVID H. TEMPLETON

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Thorium tetraiodide has a novel layer structure in the solid according to single-crystal X-ray diffraction data. The crystals are monoclinic, space group $P2_1/n$, with $a = 13.216 \pm 0.007$, $b = 8.068 \pm 0.006$, $c = 7.766 \pm 0.006$ Å., $\beta = 98.68 \pm 0.05°$, $Z = 4$, $d_x = 6.00$ g./cc. Each thorium atom has eight iodine neighbors at an average distance of 3.20 Å. at the corners of an irregular polyhedron which is approximately a square antiprism. These polyhedra share edges and triangular faces to form layers which are only weakly bonded to each other.

## Introduction

In 1950 we made and analyzed crystals of thorium tetraiodide. Weissenberg X-ray diffraction photographs of a crystal rotated about the *b*-axis showed that it is monoclinic and gave the unit cell dimensions. The space group was ambiguous because we did not have the $0k0$ data. Because of the complexity of the problem we suspended work on it. With the advent of high speed computers and improved techniques for intensity measurement we reactivated this problem and successfully determined the crystal structure.

In 1954 Jantsch, *et al.*,[2] reported on the basis of a powder diffraction pattern that $ThI_4$ might be tetragonal. D'Eye, *et al.*,[3] concluded that the crystal is orthorhombic and reported cell dimensions. In the present work we show conclusively that $ThI_4$ is monoclinic in space group $P2_1/n$. An inspection of D'Eye's published $\sin^2 \theta$ values shows them to correspond to ours, but we cannot find any significant relation of the orthorhombic cell dimensions to the monoclinic lattice which we determine. The reproduction of the powder diagram in Jantsch's paper is so poor that we cannot comment concerning his data.

## Experimental

**Preparation of Crystals.**—$ThI_4$ was prepared by heating thorium metal foil at about 500° in an iodine atmosphere in an evacuated Pyrex T-shaped tube for 1 week. The iodine was at the bottom of the tube stem at room temperature, and the thorium was in the side arm immersed in a furnace. As the $ThI_4$ was formed it distilled down the tube away from the hot reaction zone. At the higher temperatures near the reaction zone the material is orange colored, but it changes to yellow at a lower temperature. After reaction was completed the material was distilled to the other side arm and sealed off. Where the thorium foil had been there remained a gray powder which was presumably unreacted thorium and thorium oxide. As $ThI_4$ is very reactive to the atmosphere it was necessary to handle the material in a drybox; our drybox is charged with dry nitrogen.

The ampoule of $ThI_4$ was broken open, and small fragments of the yellow material were loaded into 0.3-mm. diameter vitreous silica capillaries. The capillaries were sealed and baked in a furnace at about 550°. There was enough thermal gradient to allow crystals to grow on the cooler walls of the capillary.

**X-Ray Diffraction.**—A suitable small crystal plate of dimensions approximately 0.15 × 0.10 × 0.03 mm. was attached to the wall of the capillary with its *b*-axis in the plate and along the axis of the tube. It was mounted in a goniostat on a General Electric XRD-5 apparatus equipped with a molybdenum X-ray tube, a scintillation counter, and a pulse-height discriminator. Cell dimensions and crystal settings were calculated with $\lambda\ (K\alpha_1) = 0.70926$ Å. Intensities were measured for the 1454 independent reflections permitted by the space group out to a limit of $\sin \theta/\lambda = 0.596$ ($2\theta = 50°$). Of these intensities 106 were recorded as zero. The reflections were measured by counting the peak intensity for 10 sec. The settings were verified for selected reflections by step scanning of the angle $\theta$.

The data were corrected for the Lorentz-polarization effects. These and other calculations were made with an IBM-7090 computer using the Zalkin data-processing and Fourier programs and our version of the Gantzel–Sparks–Trueblood least-squares program (all unpublished). The function minimized in least squares was $\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2$, where $w$ is the weighting factor and $F_o$ and $F_c$ are the observed and calculated structure factors. Because of the fixed-time counting technique we took the weighting factors as unity. Atomic scattering factors were taken for neutral Th and neutral I (Ibers[4]) modified for dispersion by adding −6.0 and −0.5 electrons (Templeton[5]). The imaginary dispersion terms were neglected.

**Correction for Absorption for Thin Flat Crystals.**—The data were corrected for absorption by a method which is based on experimental measurement of the absorption effect for certain reflections. This method applies to thin flat crystals mounted with the goniometer axis parallel with the plane of the crystal. We have found this technique convenient for several substances which we have studied. In the present case it accomplished a considerable reduction in the discrepancies of observed and calculated structure factors.

If the crystal is in the shape of a thin circular disk, the absorption correction depends only on the angles $P$ and $Q$ between the incident and diffracted beams, respectively, and the normal to the disk. We make the approximation that the correction depends on the harmonic mean value $m$ of $|\cos P|$ and $|\cos Q|$:

$$\frac{2}{m} = \frac{1}{|\cos P|} + \frac{1}{|\cos Q|}$$

The parameter $m$ is inversely proportional to the distance through the crystal which is traversed by a photon scattered at the center of the crystal. This procedure treats alike the

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] G. Jantsch, J. Homayr, and F. Zemek, *Monatsh.*, **85**, 526 (1954).

[3] R. W. M. D'Eye, I. F. Ferguson, and E. J. McIver, *Congr. intern. chim. pure appl., 16e Paris 1957, Mem. sect. chim. minerale,* 341 (1958).

[4] J. A. Ibers in "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. III, p. 211.

[5] D. H. Templeton in "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. III, p. 216.

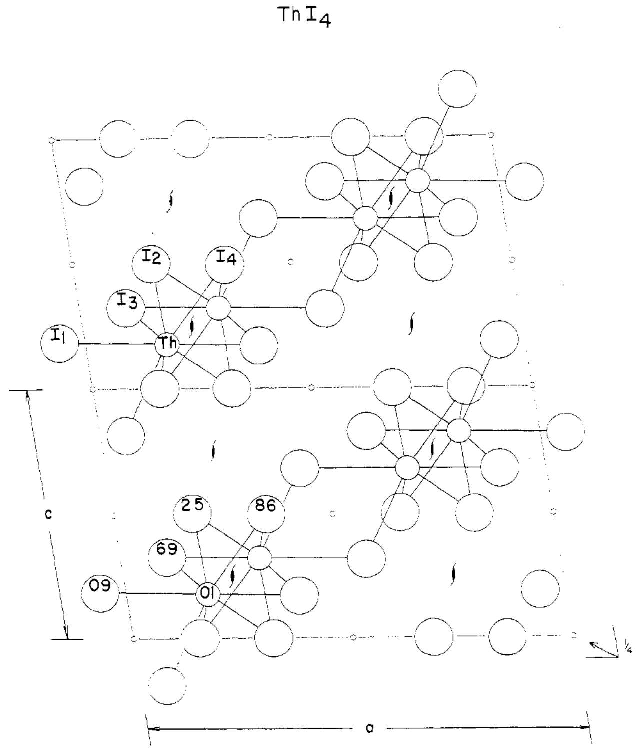

Fig. 1.—Projection of the $ThI_4$ structure onto the *ac*-plane. The numbers on atoms in the lower part of the figure are *y*-coordinates (×100).

cases in which the diffracted beam emerges from the same side or opposite side as the incident beam. The geometry of a measurement is determined by $\theta$, the Bragg angle, and $\phi$ and $\chi$, the settings of the spindle and vertical circle of the goniostat, respectively. By spherical trigonometry we have the relations

$$|\cos P| = |\cos\theta\cos\phi + \sin\theta\sin\phi\cos\chi|$$
$$|\cos Q| = |\cos\theta\cos\phi - \sin\theta\sin\phi\cos\chi|$$

if the crystal is perpendicular to the incident beam when $\theta = \phi = 0$. If the setting of $\phi$ is otherwise, a suitable constant is added to $\phi$ in the above equations.

For reflections at $\chi = 90°$, $m = |\cos P| = |\cos Q|$, and rotation of $\phi$ permits measurement of the intensities as a function of $m$ over nearly the entire range 0 to 1. These data are fitted by a convenient empirical function of $m$ which when multiplied by the measured intensities corrects them to a constant value for each reflection. This function is then used as a correction factor for the rest of the data.

In the present experiment, the function was chosen as

$$I\,(\text{corrected}) = \frac{I\,(\text{measured})}{1 + 5.25\exp(-0.69/m)}$$

The values of this correction differed by as much as a factor of 3.6.

## Results

**Unit Cell and Space Group.**—The crystals are monoclinic with unit cell dimensions: $a = 13.216 \pm 0.007$, $b = 8.068 \pm 0.006$, $c = 7.766 \pm 0.006$ Å., $\beta = 98.68 \pm 0.05°$, $V = 819$ Å.$^3$. With four formula units ($ThI_4$) per unit cell, the density calculated from the X-ray data is 6.00 g./cc.

The systematic absence of $h0l$ reflections if $h + l$ is odd and of $0k0$ reflections if $k$ is odd is characteristic of space group $P2_1/n$ ($C_{2h}^5$). This space group is confirmed by the structure determination.

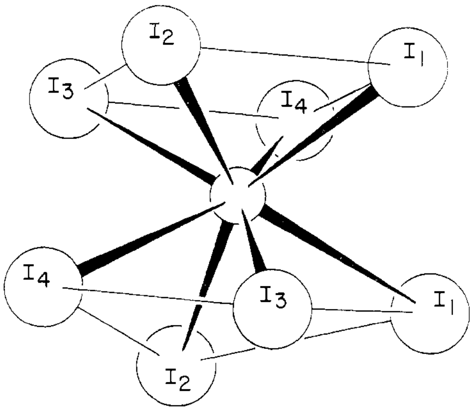

Fig. 2.—The approximately square antiprism arrangement of iodine about thorium in $ThI_4$.

Table I

Final Positional Parameters and Standard Deviations for $ThI_4$

| Atom | $x$ | $y$ | $z$ | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ |
|---|---|---|---|---|---|---|
| Th | 0.1835 | 0.0149 | 0.1769 | 0.0001 | 0.0002 | 0.0002 |
| I(1) | 0.0587 | 0.9098 | 0.8094 | 0.0002 | 0.0003 | 0.0003 |
| I(2) | 0.1801 | 0.2535 | 0.4984 | 0.0002 | 0.0003 | 0.0003 |
| I(3) | 0.0972 | 0.6917 | 0.3251 | 0.0002 | 0.0003 | 0.0003 |
| I(4) | 0.1517 | 0.3638 | 0.0014 | 0.0002 | 0.0003 | 0.0003 |

**Determination of the Structure.**—In order to obtain a trial structure we calculated a three-dimensional Patterson function. By inspection of this function with due regard to packing and interatomic distances we found a complete trial structure which accounted satisfactorily for the largest peaks. The thorium atom and all four iodine atoms in the asymmetric unit were placed in 4-fold general positions: 4(e), $\pm(x, y, z;\ {}^1/_2 - x,\ {}^1/_2 + y,\ {}^1/_2 - z)$. The positional parameters obtained from the Patterson function were all within 0.03 of the corresponding final values given in Table I.

Least-squares refinement was started using this trial structure. Each atom was given an isotropic temperature factor of the form $\exp(-B\lambda^{-2}\sin^2\theta)$, and only 622 reflections, each with unit weight, were used in the refinement. The conventional unreliability factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.16 at the end of four cycles of refinement. Encouraged by this, we calculated four further cycles using all 1454 terms, each with unit weight. This calculation resulted in $R = 0.17$.

At this stage it became apparent that the shape of the crystal, combined with the high value of the absorption coefficient, was affecting the diffracted intensity in a systematic way. An absorption correction was applied

Table II

Anisotropic Thermal Parameters (×$10^4$) and Average Root Mean Square Displacements

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | $u$, Å. |
|---|---|---|---|---|---|---|---|
| Th | 22 | 42 | 31 | −1 | 13 | 0 | 0.12 |
| I(1) | 25 | 80 | 45 | 2 | 15 | −16 | 0.14 |
| I(2) | 30 | 67 | 37 | −6 | 26 | −3 | 0.14 |
| I(3) | 25 | 68 | 82 | 3 | 25 | 15 | 0.15 |
| I(4) | 34 | 59 | 51 | −2 | 2 | 7 | 0.15 |

to the data as described earlier. After four more cycles of refinement with all the data $R$ fell to 0.120. Correction of several blunders in the data measurements and in data card punching reduced $R$ to 0.116 after four more cycles.

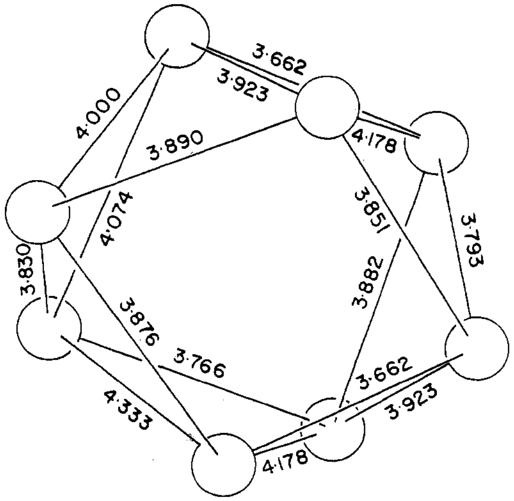

Fig. 3.—The iodine–iodine distances in the ligand polyhedron. Standard deviations of the distances are 0.005 Å.

Introduction of anisotropic thermal factors of the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}hl)$ for each of the five atoms resulted in only slight further improvement of the agreement. After four cycles with all the data, $R$ was 0.09. In the last cycle no parameter changed by more than one unit in the sixth decimal place.

The final positional parameters and their standard deviations are listed in Table I. These standard deviations are estimated by the method of least squares assuming that the discrepancies represent random errors. The anisotropic thermal parameters and the average root mean square displacements of the atoms are reported in Table II. The observed structure factor magnitudes and the calculated structure factors are shown in Table III.

A comparison of the final atomic coordinates with those obtained in the first cycles with 622 reflections revealed that no atom moved more than about 0.01 Å.

**Description of the Structure.**—The $ThI_4$ consists of layers with the iodine atoms arranged in sheets parallel to ($\bar{1}01$) and the thorium atoms located in alternate spaces between iodine sheets (Fig. 1). Each thorium atom has eight iodine neighbors arranged at the corners

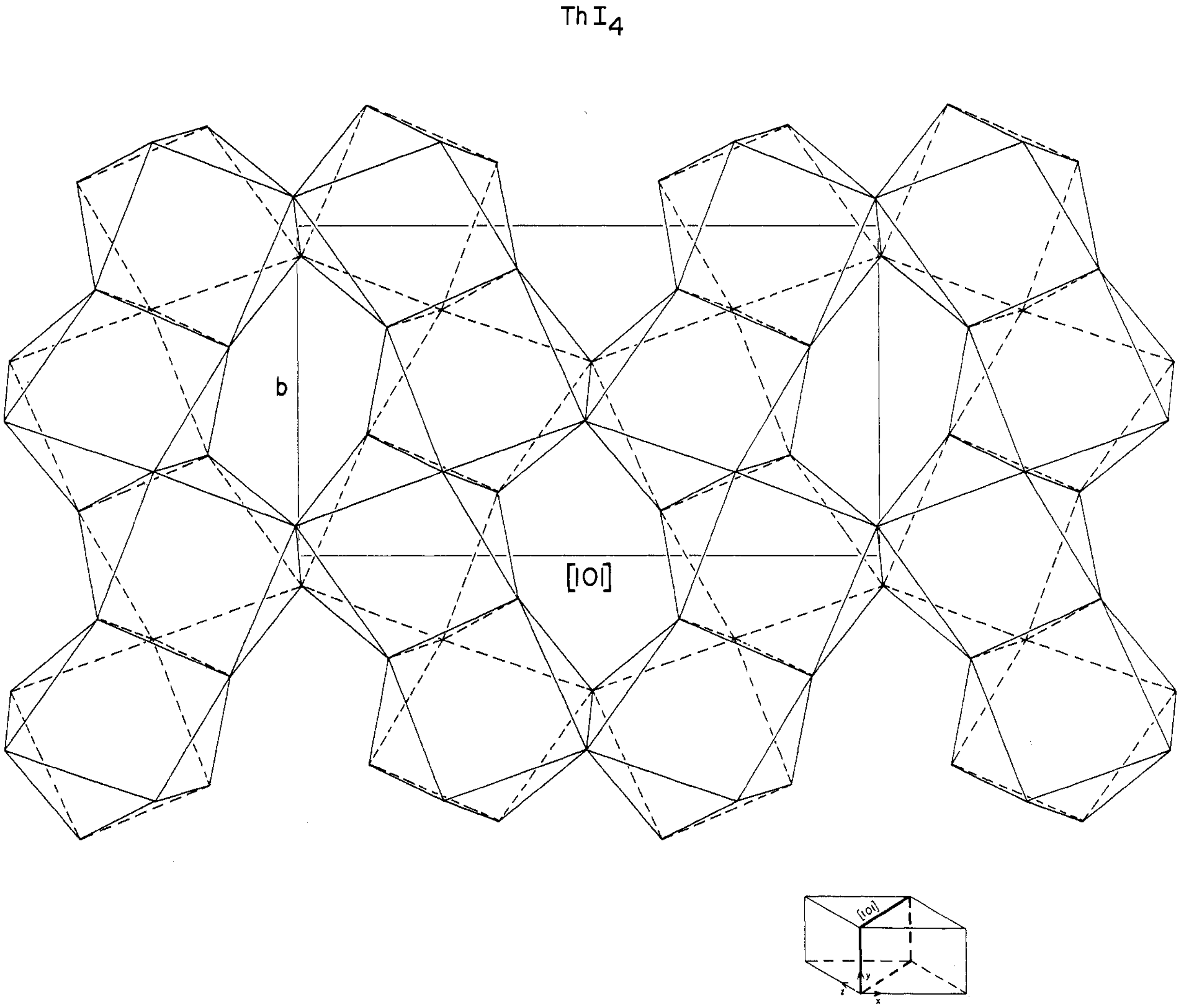

Fig. 4.—The structure of one layer of $ThI_4$, indicated by linked polyhedra. A thorium atom is at the center of each polyhedron, and an iodine atom is at each corner.

TABLE III

OBSERVED STRUCTURE FACTOR MAGNITUDES (FOB) AND CALCULATED STRUCTURE FACTORS (FCA)

```
 H,K= 0, 0
 L FOB FCA
 2  59 -56
 4 201 193
 6 534 560
 8  99 -99

 H,K= 1, 0
 L FOB FCA
-9  52 -61
-7 154 146
-5  28 -29
-3 141-123
-1 386 385
 1 224-216
 3  63 -64
 5 273 280
 7 205-212
 9  24  29

 H,K= 2, 0
 L FOB FCA
-8  49 -48
-6 211-184
-4  75 -59
-2 273-235
-0 194-191
 2 145-139
 4 137-133
 6 106-109
 8  85 -93

 H,K= 3, 0
 L FOB FCA
-9 178 172
-7  58 -64
-5  82 -69
-3 222 210
-1 146-150
 1  12   5
 3  82  82
 5  79 -78
 7   0  20

 H,K= 4, 0
 L FOB FCA
-8 117-117
-6 378-367
-4 372 366
-2 448-494
-0 304-312
 2 307 304
 4 444-476
 6   0 -10
 8  46  40

 H,K= 5, 0
 L FOB FCA
-9  95-122
-7 186-215
-5 192 178
-3 398-360
-1 209-216
 1 277 280
 3 420-433
 5  33   5
 7 102 107

 H,K= 6, 0
 L FOB FCA
-8 161 210
-6 168 182
-4 140 111
-2 334 360
-0 223 231
 2 156 150
 4 231 229
 6 168 172

 H,K= 7, 0
 L FOB FCA
-7 151 173
-5  64 -24
-3 218 223
-1 117 116
 1  69  61
 3 189 179
 5  42  49
 7  38  45

 H,K= 8, 0
 L FOB FCA
-8 127 177
-6 261-259
-4 189-178
-2 216 234
-0 380-392
 2  16   9
 4  63  60
 6 212-204

 H,K= 9, 0
 L FOB FCA
-7 109-116
-5  62 -57
-3 319 345
-1 302-317
 1  76  70
 3 214 200
 5 266-251

 H,K=10, 0
 L FOB FCA
-6  72  69
-4  44 -29
-2 169-181
-0  46  42
 2  44 -39
 4 165-158
 6  17  25

 H,K=11, 0
 L FOB FCA
-7  26   4
-5 196-183
-3 188-201
-1  24   4
 1 226-215
 3 102 -93
 5  23 -23

 H,K=12, 0
 L FOB FCA
-6 227 210
-4  98-105
-2 139 147
-0 134 133
 2  67 -61
 4 171 149

 H,K=13, 0
 L FOB FCA
-5  53-100
-3 124 131
-1 273 283
 1 156-141
 3 226 196

 H,K=14, 0
 L FOB FCA
-4  52  54
-2  24   2
-0 147-140
 2  86  80

 H,K=15, 0
 L FOB FCA
-3  89 -96
-1  38   8
 1  94  87

 H,K= 0, 1
 L FOB FCA
 1 115 107
 2 229-220
 3 507-539
 4 222 219
 5 207 214
 6  79 -75
 7  80 -83
 8  32 -35
 9 180-177

 H,K= 1, 1
 L FOB FCA
-9  30  47
-8  63 -52
-7   0  11
-6 116 102
-5  50  51
-4 278-261
-3 128 114
-2  21 -11
-1   0 -18
-0 152 150
 1  39  39
 2 394-410
 3 133 133
 4 127 134
 5  36 -36
 6  16  13
 7  18  18
 8 199-200

 H,K= 2, 1
 L FOB FCA
-9  68  65
-8 211-188
-7  25  28
-6   0 -26
-5  76 -63
-4 394-325
-3 123 107
-2 330-305
-1  27  46
-0  68 -68
 1  44 -45
 2 419-442
 3  85  88
 4 152-150
 5  62  63
 6 101-103
 7  57 -64
 8 161-175

 H,K= 3, 1
 L FOB FCA
-9  43 -27
-8 136 138
-7  69 -65
-6 171-150
-5 113 -98
-4 316 282
-3  37 -34
-2 121 104
-1  69 -68
-0  77 -78
 1 173-166
 2 307 309
 3   0   9
 4   0  18
 5  26 -36
 6  26  10
 7  71 -78
 8 123 127

 H,K= 4, 1
 L FOB FCA
-9 180 201
-8   0   3
-7 232-225
-6 270 259
-5 228 221
-4 279 261
-3 273 240
-2   0   9
-1 333-361
-0 428 463
 1 430 453
 2 176 173
 3  21  15
 4  81  80
 5 128-134
 6 227 234
 7 233 245
 8  53  50

 H,K= 5, 1
 L FOB FCA
-9   0 -29
-8 116-145
-7  45  63
-6  55  67
-5  47 -10
-4 166 142
-3  82 -64
-2 304-329
-1 181 184
-0 238 240
 1  71 -68
 2  49  27
 3  28 -25
 4 245-244
 5 126 128
 6 204 210
 7  53 -60
 8  62 -74

 H,K= 6, 1
 L FOB FCA
-8  39 -51
-7  21  53
-6  90 -92
-5  89 -85
-4 145 126
-3 139-134
-2 123-128
-1  35  28
-0   0 -31
 1  93 -93
 2  91  90
 3 148-144
 4  82 -76
 5  31  40
 6   0  15
 7  56 -61

 H,K= 7, 1
 L FOB FCA
-8  75 103
-7  72  76
-6  96-101
-5 194 164
-4 201-172
-3  15  -4
-2 102 112
-1 137 143
-0 200-202
 1 161 151
 2  88 -85
 3  43 -42
 4  34  31
 5 113 111
 6 111-112
 7  38  41

 H,K= 8, 1
 L FOB FCA
-8  22 -20
-7  60  59
-6 199-211
-5 321-280
-4  52 -16
-3 237 253
-2  99-108
-1  92 -88
-0 233-231
 1 195-190
 2  37 -28
 3 232 223
 4 129-121
 5 149-140
 6  98 -93
 7   0 -19

 H,K= 9, 1
 L FOB FCA
-8  79 100
-7 166-196
-6 179-172
-5   0  -9
-4 233 224
-3 165-177
-2  60  61
-1 227-232
-0 191-182
 1  30  31
 2 310 297
 3 201-189
 4  44 -58
 5 102 -95
 6  40 -40

 H,K=10, 1
 L FOB FCA
-7  34 -11
-6  77  73
-5 162 149
-4  56  52
-3  16   5
-2 166 180
-1  23   1
-0  89  68
 1 178 168
 2  62  62
 3   0  -2
 4  95  95
 5   0  -0
 6  51  49

 H,K=11, 1
 L FOB FCA
-7  45 -30
-6 179 157
-5  38  29
-4  97-106
-3 130 139
-2  55  50
-1  77 -75
-0 113 106
 1  93  90
 2  79 -76
 3  80  76
 4  61  53
 5  16 -33

 H,K=12, 1
 L FOB FCA
-6  42 -12
-5  92 -80
-4  81 -83
-3  98-111
-2  27   2
-1 169 169
-0   0  -4
 1 164-154
 2  33 -27
 3   0  -7
 4   0   2

 H,K=13, 1
 L FOB FCA
-6  62 -27
-5   0 -20
-4 168-186
-3 174 193
-2 152 157
-1  22  17
-0 133-131
 1   0  14
 2 107-102
 3 142 129

 H,K=14, 1
 L FOB FCA
-5  66 -61
-4  21   3
-3  67  68
-2  57 -60
-1  95 -90
-0   0  -1
 1  60 -54
 2   0  -3

 H,K=15, 1
 L FOB FCA
-3  75 -87
-2  90 -97
-1  39 -27
-0  56  63
 1 160-147

 H,K= 0, 2
 L FOB FCA
-0  33  28
 1 314-304
 2 339-338
 3  92  89
 4 180-177
 5 117 115
 6   0   7
 7 150-146
 8 213-212

 H,K= 1, 2
 L FOB FCA
-9 101 -98
-8  65  56
-7 141 129
-6 114  99
-5 124 107
-4  83  75
-3 241-218
-2 247 207
-1 326 330
-0  97  93
 1  56  44
 2 134 126
 3 154-157
 4 203 203
 5 270 278
 6   0  -6
 7  66 -73
 8  97 101

 H,K= 2, 2
 L FOB FCA
-9   0  -8
-8 256 232
-7 124 110
-6  33   7
-5 215 182
-4  75 -54
-3  53 -48
-2 447 434
-1 334 339
-0  63 -61
 1 119 112
 2  13 -16
 3  39  39
 4 321 331
 5 208 211
 6  86 -90
 7   0   6
 8  28  31

 H,K= 3, 2
 L FOB FCA
-9 107 112
-8  29 -25
-7 272-251
-6  73  64
-5 146-133
-4  28  30
-3 182 164
-2  31  31
-1 437-502
-0  90  88
 1   0 -15
 2  26 -27
 3  53  53
 4  86  84
 5 300-309
 6   0   8
 7  34  27
 8   0  -7

 H,K= 4, 2
 L FOB FCA
-8  39 -50
-7 120-116
-6  40 -31
-5 154 148
-4 237 227
-3 326-290
-2 176-182
-1  44 -47
-0 113 117
 1  75  73
 2 178 181
 3 280-281
 4 165-166
 5  40  45
 6 130 138
 7  38 -49
 8  50  50

 H,K= 5, 2
 L FOB FCA
-8 101-110
-7   0 -27
-6   0 -13
-5 249 244
-4 225-200
-3 107  83
-2 149-158
-1  17 -17
-0  16  -6
 1 308 314
 2 306-303
 3  33 -32
 4  43 -43
 5  58  58
 6  21 -42
 7 142 147
 8 140-151

 H,K= 6, 2
 L FOB FCA
-8 130-167
-7 132-150
-6  77  73
-5  42  19
-4 271-234
-3  53 -51
-2 218-237
-1 175-179
-0 101 104
 1  39  39
 2 278-274
 3 119-106
 4 124-120
 5  34 -44
 6  49  54
 7   0 -17

 H,K= 7, 2
 L FOB FCA
-8   0 -11
-7 159 180
-6  30  34
-5 298-283
-4 112  98
-3  66  58
-2  66 -62
-1 150 161
-0 149 149
 1 299-300
 2  38  31
 3 118 114
 4   0 -14
 5  32  45
 6 102 103
 7 128-130

 H,K= 8, 2
 L FOB FCA
-8 171 225
-7  38 -38
-6 102 -98
-5 100  84
-4 221 204
-3 193 208
-2 213 229
-1  51 -49
-0 151-155
 1 186 183
 2 277 267
 3 103  97
 4  74  75
 5   0  18
 6  68 -73

 H,K= 9, 2
 L FOB FCA
-8  22  -8
-7  99-109
-6  50  23
-5  97 -88
-4 194 198
-3  39  35
-2  92 -90
-1 173-180
-0 136 134
 1  21 -21
 2 149 140
 3   0  11
 4  76 -73
 5 157-142
 6 132 126

 H,K=10, 2
 L FOB FCA
-7  24  29
-6  91 -66
-5  76 -58
-4 100  99
-3  56  43
-2 111-118
-1  23 -11
-0  41 -37
 1  19 -15
 2 100  96
 3   0  -2
 4 123-108
 5   0  -9

 H,K=11, 2
 L FOB FCA
-7 119 131
-6 162-149
-5 241 225
-4   0  16
-3 107-113
-2  54 -61
-1 191 199
-0 161-158
 1 146 142
 2  32  31
 3  81 -73
 4 114-100
 5 148 133

 H,K=12, 2
 L FOB FCA
-6  67  46
-5 132-122
-4 242-264
-3  30 -18
-2 127 130
-1  70 -66
-0  51 -40
 1  93 -89
 2 199-185
 3  27 -20
 4 125 113

 H,K=13, 2
 L FOB FCA
-5 153-147
-4  21  16
-3  31  26
-2  68  74
-1  42 -36
-0 142-133
 1 138-133
 2  80  73
 3  71  63

 H,K=14, 2
 L FOB FCA
-4  75  69
-3  27  35
-2  89 104
-1  29  15
-0   0  -8
 1  49  51
 2  76  70

 H,K=15, 2
 L FOB FCA
-3  39  27
-2 115 123
-1 116-114
-0   0  17

 H,K= 0, 3
 L FOB FCA
 1 175 166
 2 114-106
 3  22  18
 4 126 122
 5 149 150
 6  98 -97
 7  74  68
 8   0  -0

 H,K= 1, 3
 L FOB FCA
-8  27  11
-7  23 -20
-6 224 212
-5 228-210
-4 125-114
-3 307-275
-2 102  88
-1  48  10
-0 279 288
 1 391-414
 2 159-156
 3 150-137
 4 151 150
 5  57 -59
 6 109 111
 7 225-233
 8  78 -80

 H,K= 2, 3
 L FOB FCA
-8   0 -13
-7 183 162
-6  34  38
-5 353-314
-4  41  36
-3 150 121
-2  58  49
-1 156 157
-0  19  21
 1 405-429
 2  24  15
 3 207 210
 4 101 101
 5   0  -0
 6  39 -39
 7 186-199
 8  46  44

 H,K= 3, 3
 L FOB FCA
-8  29  21
-7  38 -34
-6 333-302
-5 215 184
-4 125 106
-3 199-184
-2 119-109
-1  84  89
-0 380-410
 1 114 114
 2 166 169
 3 146-147
 4 174-175
 5  99 101
 6 189-200
 7   0  -3
 8  93  91

 H,K= 4, 3
 L FOB FCA
-8 145-152
-7 153-146
-6   0  12
-5  38  43
-4 143-128
-3 134-122
-2 163-171
-1 166-177
-0  74  75
 1  65  61
 2 229-229
 3 151-152
 4  18 -20
 5  94 -99
 6   0  14
 7  30  46
 8 116-119

 H,K= 5, 3
 L FOB FCA
-8  71 -87
-7  23  37
-6  38  43
-5 252 252
-4  96  82
-3   0   6
-2 113-120
-1 170 176
-0  86  90
 1 241 242
 2  45  40
 3  26  -7
 4  83 -82
 5 191 192
 6  90  91
 7  49  56

 H,K= 6, 3
 L FOB FCA
-8  57  62
-7 106 128
-6  85 103
-5 197 183
-4 102  84
-3 212-208
-2  56  63
-1 261 279
-0 185 191
 1 126 123
 2  11  -3
 3 140-136
 4  82  83
 5 231 229
 6  94  94
 7   0   1

 H,K= 7, 3
 L FOB FCA
-8 140 183
-7 187-221
-6  87  93
-5 125 -90
-4 200-168
-3  48 -42
-2 337 372
-1 265-288
-0  30  14
 1  41 -40
 2  90 -86
 3 117-111
 4 302 292
 5 138-129
 6  40 -42
 7  31 -35

 H,K= 8, 3
 L FOB FCA
-8  39 -43
-7  38 -28
-6  70 -54
-5  77 -64
-4 138 131
-3 199 211
-2 165-173
-1 111-109
-0  45  41
 1  27  -9
 2  64  61
 3 167 161
 4 145-142
 5  95 -95
 6  62  69

 H,K= 9, 3
 L FOB FCA
-7  46 -23
-6 113 -91
-5  75  53
-4   0  26
-3  88  89
-2  96-104
-1  63 -61
-0  78 -82
 1 109 103
 2  23  17
 3   0 -16
 4 111-104
 5   0  -7
 6  48 -38

 H,K=10, 3
 L FOB FCA
-7 158-177
-6 129-123
-5  73  52
-4   0 -12
-3  38 -43
-2 138-150
-1 198-207
-0  86 -79
 1  71  69
 2   0  -1
 3 104 -97
 4 134-124
 5 108-100

 H,K=11, 3
 L FOB FCA
-6 183 158
-5  84 -56
-4  55 -61
-3  88  95
-2 169-179
-1  51  47
-0 196 189
 1   0   8
 2 133-123
 3  73  67
 4  83 -72

 H,K=12, 3
 L FOB FCA
-6   0 -19
-5 114 -96
-4 134 140
-3  31 -22
-2 159 175
-1 180 181
-0  43 -44
 1 130-122
 2 178 169
 3  23  33
 4  62  57

 H,K=13, 3
 L FOB FCA
-5  92 -94
-4  68  62
-3  26   4
-2 105 111
-1  86 -89
```

of an irregular polyhedron which is approximately a square antiprism (Fig. 2). The Th–I distances (Table IV) range from 3.128 to 3.291 Å. with a mean value of 3.202 Å. The I–I distances in the "antiprism" are shown in Fig. 3 and range from 3.662 to 4.178 Å. for nearest neighbors. One of the square faces of the polyhedron is very nearly planar, but the other is considerably more distorted both within and out of the plane. The angles at the corners of these faces are listed in Table V.

The ligand polyhedra are linked together by sharing edges (I(1) pairs) and triangular faces (I(2)–I(3)–I(4) faces) as shown in Fig. 4. Each Th has two Th neighbors at 4.478 ± 0.005 Å., in the directions of the shared faces. The only close contact between iodine atoms in the same layer, other than the edges of the ligand polyhe-

TABLE III (*Continued*)

```
-0  59 -44
 1  45 -40
 2  91  85
 3   0   7

 H,K=14, 3
 L FOB FCA
-4  31 -44
-3  98 102
-2  36  30
-1   0  -4
-0  94 -86
 1   0  15

 H,K= 0, 4
 L FOB FCA
-0 153 157
 1  61 -55
 2  74 -73
 3  45  39
 4  56 -54
 5   0  -2
 6 123 120
 7  43 -39
 8  55 -55

 H,K= 1, 4
 L FOB FCA
-8   0  -4
-7  91  89
-6  60  60
-5 244-227
-4 244-226
-3 196-171
-2 139 111
-1  98  86
-0  31  -6
 1 331-351
 2 233-236
 3  77 -79
 4 154 156
 5  31  12
 6  95-100
 7 185-200
 8  45 -47

 H,K= 2, 4
 L FOB FCA
-8 124 107
-7  83 -75
-6 104 -94
-5  23 -30
-4 235-192
-3 102  76
-2 258 235
-1 106-111
-0 237-253
 1  64 -64
 2  61 -58
 3 100  99
 4 164 166
 5  95 -99
 6 187-202
 7  26 -26
 8  30  48

 H,K= 3, 4
 L FOB FCA
-8 154-148
-7 162 158
-6 146 125
-5  59  47
-4  23  23
-3 449 431
-2 233-221
-1 160 168
-0 225 236
 1 129 126
 2  91 -96
 3 408 426
 4  83 -85
 5  25  37
 6 103 103
 7 128 134

 H,K= 4, 4
 L FOB FCA
-8  41 -12
-7  27  22
-6  25  13
-5  32  41
-4 205 189
-3 103 -86

-2  28 -19
-1 125 133
-0  19  33
 1  41 -39
 2 192 193
 3  50 -51
 4  42 -39
 5 113 118
 6  23  30
 7  54 -61

 H,K= 5, 4
 L FOB FCA
-8  51 -66
-7  77 -88
-6  82  79
-5  69  71
-4 114  94
-3 325-301
-2 114-115
-1  38 -32
-0 169 180
 1  22   9
 2  20   3
 3 249-247
 4  14 -15
 5   0   9
 6  95  99
 7   0 -25

 H,K= 6, 4
 L FOB FCA
-8  34 -48
-7  51  63
-6 195 214
-5   0  -5
-4 205-169
-3  61 -58
-2  45  31
-1 137 144
-0 187 190
 1  52 -42
 2 229-229
 3  45 -41
 4 102 104
 5 115 116
 6  43  46
 7  48 -58

 H,K= 7, 4
 L FOB FCA
-7  84  86
-6 173-181
-5 167-144
-4 167 144
-3 138-140
-2  50 -49
-1 102 103
-0 147-143
 1 246-248
 2 123 121
 3  50 -47
 4  64 -67
 5  34  34
 6  33 -37

 H,K= 8, 4
 L FOB FCA
-7 102-117
-6 180-180
-5 134 112
-4 137-124
-3  68 -65
-2  29 -19
-1 115-118
-0 199-206
 1 158 154
 2  95 -84
 3 132-127
 4   0  -4
 5  22 -21
 6 136-132

 H,K= 9, 4
 L FOB FCA
-7  58 -53
-6  92 -68
-5 193 175
-4  39  34
-3 169 185
-2  15 -15
-1  34 -31
-0  41 -43

 1 206 210
 2   0  22
 3 121 113
 4  46 -47
 5   0   5

 H,K=10, 4
 L FOB FCA
-6 136 124
-5  75  59
-4 216 215
-3  31  -5
-2  97-100
-1  84 -89
-0 220 224
 1 106 103
 2 125 120
 3  56 -55
 4  53 -52
 5  29 -20

 H,K=11, 4
 L FOB FCA
-6  61  27
-5  76  67
-4  79 -77
-3 168-186
-2 107 118
-1   0   8
-0   0   3
 1  39  42
 2  21 -25
 3 171-155
 4  72  61

 H,K=12, 4
 L FOB FCA
-5 104 -89
-4  62 -58
-3 165 182
-2  24  37
-1  82 -81
-0  64  57
 1  22 -15
 2  75 -71
 3 126 120

 H,K=13, 4
 L FOB FCA
-4  32   7
-3  74  76
-2  18 -17
-1  34 -21
-0   0 -18
 1  84 -85
 2  37  34

 H,K=14, 4
 L FOB FCA
-2  66 -81
-1  30 -16
-0 195-187

 H,K= 0, 5
 L FOB FCA
 1 164 162
 2  78 -70
 3 122-123
 4  92  90
 5 137 135
 6   0 -30
 7  93  88

 H,K= 1, 5
 L FOB FCA
-7 174 162
-6  60  52
-5  98  90
-4 218-203
-3 220 206
-2 361 318
-1 272 261
-0  98 -98
 1  79  80
 2 109-112
 3 247 261
 4 231 237
 5 140 146
 6 105-113
 7  46  51

 H,K= 2, 5
 L FOB FCA

-7 101  87
-6  53 -56
-5 204-169
-4  91  75
-3 104  90
-2   0  12
-1   0   7
-0  70 -64
 1 179-189
 2  91  93
 3 152 158
 4  29  -8
 5  92 -92
 6  50 -43
 7  65 -69

 H,K= 3, 5
 L FOB FCA
-7  97 -82
-6 110 -92
-5 121 109
-4 130-115
-3  74 -69
-2 214 194
-1  36 -38
-0 222-229
 1 103 105
 2  27 -13
 3  80 -77
 4  93 103
 5   0  12
 6 168-183
 7  54  38

 H,K= 4, 5
 L FOB FCA
-7 135-137
-6 126 118
-5   0  15
-4  32  25
-3  90  63
-2  30  -9
-1 211-218
-0 150 148
 1  35  33
 2  44 -34
 3  51  52
 4  32  28
 5 167-175
 6  68  70
 7  46  57

 H,K= 5, 5
 L FOB FCA
-7  80 -83
-6 199 214
-5 107-100
-4 114 -94
-3 241-216
-2 167-172
-1  90 -92
-0 256 271
 1 153-156
 2 162-160
 3 189-196
 4  35 -40
 5  47 -38
 6 118 126

 H,K= 6, 5
 L FOB FCA
-7 132 156
-6  76 -87
-5  34  11
-4 153-141
-3 113-108
-2  38 -36
-1 264 288
-0 111-109
 1 101-107
 2 128-136
 3   0   2
 4   0  -1
 5 189 189
 6  77 -84

 H,K= 7, 5
 L FOB FCA
-7  52  54
-6 130 126
-5  95  74
-4  74 -76
-3 216 226

-2  51  61
-1  39  39
-0 113 111
 1 125 128
 2  94 -98
 3 163 155
 4 127 121
 5  23  29
 6   0  -1

 H,K= 8, 5
 L FOB FCA
-6  36 -12
-5 109 -92
-4 141 133
-3  37  30
-2  41 -42
-1  90  93
-0  55  55
 1 129-131
 2  94 101
 3  70  66
 4  38 -34
 5  29  32

 H,K= 9, 5
 L FOB FCA
-6 143-130
-5  50  25
-4 208 204
-3  45 -27
-2 115-129
-1  36 -36
-0  73 -70
 1  47  60
 2 139 135
 3  48 -39
 4 108-105

 H,K=10, 5
 L FOB FCA
-6 108  95
-5 220 192
-4  61  56
-3 170-187
-2  49  37
-1  62 -65
-0 106 107
 1 162 160
 2  30  25
 3 209-203
 4  23  22

 H,K=11, 5
 L FOB FCA
-5 108-106
-4  46 -21
-3  57 -48
-2  83 -85
-1  16  -4
-0  75  71
 1 113-114
 2  79 -74
 3  33 -31

 H,K=12, 5
 L FOB FCA
-4  92 -91
-3  58 -52
-2  40 -40
-1  44  40
-0 179-173
 1  52  51
 2  41 -39

 H,K=13, 5
 L FOB FCA
-3  72  80
-2 119 127
-1  30  -6
-0  62 -50

 H,K= 0, 6
 L FOB FCA
-0  72  67
 1 139-142
 2 122-119
 3   0  19
 4 109-105
 5  85  84
 6  67  59
 7  92 -93

 H,K= 1, 6
 L FOB FCA
-7 220 206
-6 150-146
-5 118-109
-4  35  22
-3  80  69
-2  47 -16
-1 261 236
-0 213-217
 1 136-148
 2  60  57
 3 152 165
 4  62 -57
 5 101 100
 6 135-136
 7  49 -50

 H,K= 2, 6
 L FOB FCA
-7 122 -98
-6   0   2
-5  75 -67
-4  51 -48
-3  85 -65
-2 260 241
-1 155-157
-0 102-106
 1  51 -52
 2  48  55
 3  82 -87
 4 141 158
 5 116-123
 6  95-104

 H,K= 3, 6
 L FOB FCA
-7  53 -40
-6 108 -98
-5 268-246
-4  63  66
-3  24  -7
-2  52 -56
-1 118-126
-0  95 -96
 1 264-285
 2  76  75
 3  65  66
 4  59 -68
 5 175-188
 6   0 -22

 H,K= 4, 6
 L FOB FCA
-7  29   9
-6  62 -54
-5 164 163
-4  94  82
-3  56 -44
-2  58 -60
-1  52  56
-0  82 -78
 1 174 182
 2 103 108
 3  42 -49
 4  73 -76
 5  64  75
 6  44 -38

 H,K= 5, 6
 L FOB FCA
-6 100 106
-5 228 229
-4  90 -78
-3 150-135
-2 184 190
-1 173 185
-0  99  93
 1 136 139
 2  55 -57
 3  81 -65
 4 162 170
 5 139 143
 6  31  31

 H,K= 6, 6
 L FOB FCA
-6 111 113
-5  62 -44
-4 248-216
-3 139 131
-2   0   8
-1  15  14

-0  63  70
 1   0 -27
 2 210-224
 3 128 130
 4  81  85
 5   0 -12

 H,K= 7, 6
 L FOB FCA
-6  25 -26
-5  48   2
-4  48 -32
-3  68 -63
-2  41  31
-1 137 158
-0  47 -48
 1  60 -66
 2   0 -15
 3  15  12
 4   0   4
 5 110 111

 H,K= 8, 6
 L FOB FCA
-6  46  47
-5  84 -82
-4  54  36
-3  40  23
-2 149 161
-1 142-153
-0  29  29
 1  62 -68
 2  37  27
 3  22  -8
 4 137 140

 H,K= 9, 6
 L FOB FCA
-5  43   5
-4  26 -16
-3  28  -5
-2 159-170
-1 202-215
-0  57  50
 1  34  35
 2  49 -49
 3  55 -53
 4 110-104

 H,K=10, 6
 L FOB FCA
-5   0 -14
-4  43  46
-3  62 -62
-2 206-236
-1 122 132
-0 106  99
 1  52 -45
 2  48 -45
 3  23 -22

 H,K=11, 6
 L FOB FCA
-4  34  13
-3  28 -26
-2  62  67
-1  74  73
-0  23  22
 1  96  99
 2  24  23

 H,K=12, 6
 L FOB FCA
-2  32 -43
-1  70  78
-0  42  41

 H,K= 0, 7
 L FOB FCA
 1  74 -83
 2  94 -92
 3 127-125
 4  93  92
 5  68 -61
 6  32 -14

 H,K= 1, 7
 L FOB FCA
-6  68  54
-5 129-124
-4 181-174
-3 104 107
-2  40  27

-1 207-193
-0  41  -4
 1  52 -55
 2 121-135
 3  65  66
 4  49  31
 5 137-155
 6  36 -28

 H,K= 2, 7
 L FOB FCA
-6   0  -3
-5 173-153
-4 182 159
-3 136 124
-2  63  56
-1 123 135
-0  41  42
 1 163-181
 2 158 179
 3 169 190
 4  33   5
 5  36  19

 H,K= 3, 7
 L FOB FCA
-6  43 -44
-5  41  23
-4 127 113
-3 151 135
-2 133 124
-1  92 -99
-0  89 -91
 1  74  82
 2 175 192
 3  59  70
 4  54  60
 5  73 -85

 H,K= 4, 7
 L FOB FCA
-6  50 -25
-5 112 102
-4  58 -60
-3  38  40
-2 192-190
-1  35  39
-0   0  -9
 1 103 113
 2  74 -80
 3  43  48
 4 129-154
 5   0  14

 H,K= 5, 7
 L FOB FCA
-5  93 -83
-4   0  10
-3   0  -2
-2  63 -64
-1 149 164
-0  77  79
 1 110-119
 2  21 -31
 3  49  54
 4  16 -17
 5  60  74

 H,K= 6, 7
 L FOB FCA
-5  38  14
-4  29  -1
-3 249-245
-2 128 139
-1  71  75
-0 101-100
 1  75 -82
 2  50  58
 3 158-165
 4  72  75

 H,K= 7, 7
 L FOB FCA
-5 146-128
-4 211-186
-3  38 -32
-2  67  66
-1  45 -41
-0  63 -59
 1 115-124
 2 168-178
 3  16  16
 4  92  89

 H,K= 8, 7
 L FOB FCA
-4  91  76
-3  64  60
-2  67  68
-1  46 -48
-0  39 -41
 1  41 -33
 2  99 104
 3  64  60

 H,K= 9, 7
 L FOB FCA
-4  94  96
-3  36 -44
-2  32 -33
-1  65  71
-0  33  38
 1 123 125
 2  66  65

 H,K=10, 7
 L FOB FCA
-3  30  33
-2  26  -7
-1  39 -23
-0   0  19
 1 144 152

 H,K= 0, 8
 L FOB FCA
-0 161 160
 1  36 -15
 2 124 121
 3  27  -8
 4  98 104
 5   0  21

 H,K= 1, 8
 L FOB FCA
-5  51  26
-4  63  44
-3  97 -88
-2  98  89
-1 117 106
-0  81 -83
 1   0  -7
 2  79  86
 3  66 -64
 4  46  22

 H,K= 2, 8
 L FOB FCA
-5  30   7
-4 193-167
-3 212 192
-2 125 115
-1 114-116
-0 162-169
 1  87  98
 2 102-113
 3 114 129
 4  74  79

 H,K= 3, 8
 L FOB FCA
-5  44  -7
-4 111 101
-3 141 130
-2  83 -66
-1 117-122
-0   0  -2
 1  15  31
 2 105 119
 3  90 100
 4  93-109

 H,K= 4, 8
 L FOB FCA
-4  28 -21
-3  72 -54
-2 126-120
-1  34 -27
-0  35 -18
 1  15 -16
 2  35 -39
 3  52 -61
 4  92 -98

 H,K= 5, 8
 L FOB FCA
-4 135-114

-3  92 -75
-2  58  48
-1  82 -80
-0  27 -40
 1   0  -1
 2  67 -68
 3  62 -64

 H,K= 6, 8
 L FOB FCA
-4   0  30
-3  45  44
-2  28  38
-1  48  55
-0 234 231
 1 132-149
 2   0  -7
 3  73  79

 H,K= 7, 8
 L FOB FCA
-3  68  60
-2  86  93
-1 151 164
-0 117-118
 1  83 -90
 2  52  58

 H,K= 8, 8
 L FOB FCA
-2  19 -26
-1  31   6
-0 125-119
 1  41  55

 H,K= 0, 9
 L FOB FCA
 1  59  45
 2  40   6
 3  81 -85

 H,K= 1, 9
 L FOB FCA
-3  85  75
-2   0   1
-1   0   7
-0  49  49
 1  55 -60
 2  89 -97
 3  63  55

 H,K= 2, 9
 L FOB FCA
-3  44  20
-2  91 -92
-1  46  26
-0 252-260
 1  69 -71
 2  76  79

 H,K= 3, 9
 L FOB FCA
-2   0  22
-1 113-121
-0  44 -48
 1  91 100
 2  86  96

 H,K= 4, 9
 L FOB FCA
-2 114 117
-1  67 -78
-0  95  95
 1  70  81

 H,K= 5, 9
 L FOB FCA
-1  52  61
-0  48  47
```

dron, is between I(3)–I(4) pairs at 3.864 ± 0.005 Å. Each iodine atom has two Th neighbors.

TABLE IV

DISTANCES TO NEAREST NEIGHBORS OF THORIUM

| Atom | Distances,[a] Å. |
|---|---|
| I(1) | 3.188, 3.276 |
| I(2) | 3.159, 3.208 |
| I(3) | 3.134, 3.232 |
| I(4) | 3.128, 3.291 |

[a] Each standard deviation is 0.004 Å.

The packing of the iodine atoms in the layers is not simple. Parts of the structure are very similar to the packing of triangles, squares, and pentagons in the

TABLE V

ANGLES OF THE "SQUARE" FACES OF THE LIGAND POLYHEDRON

| Face 1 | | Face 2 | |
|---|---|---|---|
| I(4)–I(1)–I(2) | 87.0° | I(2)–I(1)–I(3) | 76.5° |
| I(1)–I(2)–I(3) | 91.5° | I(1)–I(3)–I(4) | 101.5° |
| I(2)–I(3)–I(4) | 91.4° | I(3)–I(4)–I(2) | 79.5° |
| I(3)–I(4)–I(1) | 90.0° | I(4)–I(2)–I(1) | 98.0° |

TABLE VI

IODINE–IODINE DISTANCES BETWEEN LAYERS

| Atoms | Distance,[a] Å. |
|---|---|
| I(1)–I(2) | 4.155 |
| I(1)–I(3) | 4.252 |
| I(2)–I(3) | 4.125 |
| I(2)–I(4) | 4.079 |

[a] Standard deviations are 0.006 Å. or less.

oxygen sheets in the $BaTi_4O_9$ structure,[6] but the stacking of these sheets is quite different. We know of no other substance with a structure which resembles the entire arrangement.

The layers are bonded together only by weak forces. The I–I contacts between layers (Table VI) all exceed 4.07 Å. The orientation of these layers conforms to the platy $\{10\bar{1}\}$ habit of the crystals.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
LAFAYETTE COLLEGE, EASTON, PENNSYLVANIA

# The Interaction between Ammonium Fluoride and Metal Fluorides as Compressed Powders

BY DAVID S. CROCKET, III, AND ROBERT A. GROSSMAN

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Finely powdered mixtures of metal fluorides interact with $NH_4F$ to form double salts of the type $NH_4MF_3$ (where M = $Co^{+2}$, $Cu^{+2}$, $Mn^{+2}$, $Cd^{+2}$, $Ni^{+2}$, or $Zn^{+2}$) at pressures of 100,000 p.s.i. at 25°. In the case of Co, Cu, Ni, and Zn compounds heating to 110° caused the formation of $(NH_4)_2MF_4$ type compounds which are isostructural with $K_2NiF_4$.

## Introduction

The interchange of anions in powdered mixtures subjected to pressure has been shown by Meloche and Kalbus,[1] Ketelaar,[2] and others. Nonnenmacher and Merke[3] have also shown that complex ions can be formed under pressure in the formation of KBr disks used in infrared spectral determinations.

With this in mind it was decided to investigate a series of known fluoride double salts as to the interaction of powdered mixtures of their components under various conditions of temperature and pressure.

## Experimental

**Reagents.**—The $NH_4F$ used throughout was J. T. Baker or Mallinckrodt analytical grade reagent. It was further purified by dissolving in methyl alcohol and reprecipitating by the addition of ether. Cobalt(II) fluoride and manganese(II) fluoride were prepared by the reaction of the carbonates with HF followed by oven heating to remove water. The infrared spectra of these compounds showed them to be anhydrous. Copper(II) fluoride and nickel fluoride were formed by reaction of the metal bromide with $ClF_3$ at 250–300°.[4] X-Ray diffraction patterns gave lines attributable only to the fluorides.

**Complex Fluorides.**—The known fluoride complexes $NH_4ZnF_3$, $NH_4CoF_3$, $NH_4CuF_3$, $NH_4CdF_3$, and $NH_4MnF_3$ for comparison purposes were prepared by reaction of the metal bromides with ammonium fluoride in methyl alcohol as fully described by Haendler, *et al.*[5]

**Analytical.**—Copper, zinc, nickel, and cobalt were determined using standard EDTA titrations.

Ammonia was determined by distillation from strongly alkaline solutions into cold boric acid solution, followed by titration with hydrochloric acid, using brom cresol green indicator.

Fluorine was determined by distillation from sulfuric acid solution[6] followed by titration of aliquots of distillate with cerium(III) chloride, using murexide indicator.[7]

Infrared spectra were determined using a Beckman IR-5 spectrophotometer with sodium chloride optics. Samples were run as Halocarbon mulls[8] on calcium fluoride plates.

X-Ray diffraction patterns were taken using a G.E. RDX-5 diffractometer with filtered copper K$\alpha$ and iron K$\alpha$ radiation.

**Procedure for Determination of Complex Formation in the Mixtures of $NH_4F$ and Metal Fluorides.**—The particular metal fluoride involved was well ground with a large excess of ammonium fluoride in an agate mortar and pestle. The mixture was then placed in a die constructed of a 0.5-in. i.d. steel bushing[9] and two hardened steel pins, one 0.5 in. long, the other 2.5 in. long; the diameter was such as just to allow passage through the bushing. The mixture was then pressed into a pellet by subjecting it to a pressure of about 100,000 p.s.i. in a Carver 10-ton bench press. Depending upon the circumstances the pellet was held at this pressure for a certain length of time or removed immediately. Again depending upon the purpose of the particular run the pellet might or might not be heated. The pellet was then reground, leached with methyl alcohol to remove the unchanged ammonium fluoride, and dried with anhydrous ether. Since the complex fluorides are very insoluble in methyl alcohol, and the metal fluorides are for the most part insoluble in methyl alcohol also, these remained as a residue. The formation of any complex was then shown from a comparison of the infrared spectrum or X-ray powder pattern of the residue with that of an authentic sample, and the amount of complex formed could be determined from an ammonia analysis, since the only ammonium ion remaining in the residue was tied up in the complex.

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