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THE CRYSTAL STRUCTURE OF THORIUM TETRAIODIDE

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THE CRYSTAL STRUCTURE OF THORIUM TETRAIODIDE

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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

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., $\beta = 98.68 \pm 0.05^{\circ}$, $Z = 4$, $d_x = 6.00$ g./cc. Each thorium atom has 8 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 a 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 grey 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 dry box; our dry box is charged with dry nitrogen.

The ampule 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 X 0.10 X 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 $\sin\theta/\lambda = 0.596$ ($2\theta = 50^\circ$). Of these intensities 106 were recorded as zero. The reflections were measured by counting the peak intensity for 10 seconds. The settings were verified for selected reflections by step scanning of the angle θ.

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 $\sum w(|F_o|-|F_c|)^2/\sum wF_o^2$, 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 $\underline{P}$ and $\underline{Q}$ 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 $\underline{m}$ of $|\cos\underline{P}|$ and $|\cos\underline{Q}|$:

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

The parameter $\underline{m}$ 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 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 θ, the Bragg angle, and ϕ and χ, the settings respectively of the spindle and vertical circle of the goniostat. By spherical trigonometry we have the relations:

$$|\cos\underline{P}| = |\cos\theta\cos\phi + \sin\theta\sin\phi\cos\chi|,$$

$$|\cos\underline{Q}| = |\cos\theta\cos\phi - \sin\theta\sin\phi\cos\chi|,$$

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

For reflections at $\chi = 90^\circ$, $\underline{m} = |\cos\underline{P}| = |\cos\underline{Q}|$, and rotation of ϕ permits measurement of the intensities as a function of $\underline{m}$ over nearly the entire range 0 to 1. These data are fitted by a convenient empirical function of $\underline{m}$ 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:

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

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:

$$a = 13.216 \pm 0.007,\ b = 8.068 \pm 0.006,\ c = 7.766 \pm 0.006\ \text{Å.},$$
$$\beta = 98.68 \pm 0.05^{\circ},\ V = 819\ \text{Å}^3.$$

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 $h0\ell$ reflections if $h + \ell$ 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.

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:

$$4(e),\quad \pm(x,\ y,\ z;\ \tfrac{1}{2} - x,\ \tfrac{1}{2} + y,\ \tfrac{1}{2} - z).$$

The positional parameters obtained from the Patterson function were all within 0.03 of the corresponding final values given in Table I.

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)	.0587	.9098	.8094	.0002	.0003	.0003
I(2)	.1801	.2535	.4984	.0002	.0003	.0003
I(3)	.0972	.6917	.3251	.0002	.0003	.0003
I(4)	.1517	.3638	.0014	.0002	.0003	.0003

Least-squares refinement was started using this trial structure. Each atom was given an isotropic temperature factor of the form $\exp(-\underline{B}\lambda^{-2}\sin^2\theta)$, and only 622 reflections, each with unit weight, were used in the refinement. The conventional unreliability factor $\underline{R} = \sum ||\underline{F_o}|-|\underline{F_c}|| / \sum |\underline{F_o}|$ was 0.16 at the end of 4 cycles of refinement. Encouraged by this, we calculated 4 further cycles using all 1454 terms, each with unit weight. This calculation resulted in $\underline{R} = 0.17$.

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 to the data as described earlier. After 4 more cycles of refinement with all the data $\underline{R}$ fell to 0.120. Correction of several blunders in the data measurements and in data card punching reduced $\underline{R}$ to 0.116 after 4 more cycles.

Introduction of anisotropic thermal factors of the form $\exp(-\beta_{11}\underline{h}^2 - \beta_{22}\underline{k}^2 - \beta_{33}\underline{\ell}^2 - 2\beta_{12}\underline{hk} - 2\beta_{13}\underline{h\ell} - 2\beta_{23}\underline{k\ell})$ for each of the five atoms resulted in only slight further improvement of the agreement. After 4 cycles with all the data, $\underline{R}$ was 0.09. In the last cycle no parameter changed by more than one unit in the 6th 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.

TABLE II

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) AND AVERAGE ROOT MEAN SQUARE DISPALCEMENTS

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$\underline{u}$, Å.
Th	22	42	31	-1	13	0	0.12
I(1)	25	80	45	2	15	-16	.14
I(2)	30	67	37	-6	26	-3	.14
I(3)	25	68	82	3	25	15	.15
I(4)	34	59	51	-2	2	7	.15

TABLE III

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

(Table submitted in two parts as photographic prints.)

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 8 iodine neighbors arranged at the corners 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

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.

Table III page 1

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
-6 168 102
-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
-0 300-392
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
-3 180-201
-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 85 -96
-1 30 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
2 354-410
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
-8 211-108
-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 -66
-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 20 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
-5 153-167
-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
5 130-129
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

Table III page 2

-0 59 -44	-2 28 -19	1 206 210	-7 101 87
1 45 -40	-1 125 133	2 0 22	-6 53 -56
2 91 85	-0 19 33	3 121 113	-5 204-169
3 0 7	1 41 -39	4 46 -47	-4 91 75
	2 192 193	5 0 5	-3 104 90
H,K=14, 3	3 50 -51		-2 0 12
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-4 31 -44	5 113 118	L FOB FCA	-0 70 -64
-3 98 102	6 23 30	-6 136 124	1 179-189
-2 36 30	7 54 -61	-5 75 59	2 91 93
-1 0 -4		-4 216 215	3 152 158
-0 94 -86	H,K= 5, 4	-3 31 -5	4 29 -8
1 0 15	L FOB FCA	-2 97-100	5 92 -92
	-8 51 -66	-1 84 -89	6 50 -43
H,K= 0, 4	-7 77 -88	-0 220 224	7 65 -69
L FOB FCA	-6 82 79	1 106 103	
-0 153 157	-5 69 71	2 125 120	H,K= 3, 5
1 161 -55	-4 114 94	3 56 -55	L FOB FCA
2 74 -73	-3 325-301	4 53 -52	-7 97 -82
3 45 39	-2 114-115	5 29 -20	-6 110 -92
4 56 -54	-1 38 -32		-5 121 109
5 0 -2	-0 169 180	H,K=11, 4	-4 130-115
6 123 120	1 22 9	L FOB FCA	-3 74 -69
7 43 -39	2 20 3	-6 61 27	-2 214 194
8 55 -55	3 249-247	-5 76 67	-1 36 -38
	4 14 -15	-4 79 -77	-0 222-229
H,K= 1, 4	5 0 9	-3 168-186	1 103 105
L FOB FCA	6 95 99	-2 107 118	2 27 -13
-8 0 -4	7 0 -25	-1 0 8	3 80 -77
-7 91 89		-0 0 3	4 93 103
-6 60 60	H,K= 6, 4	1 39 42	5 0 12
-5 244-227	L FOB FCA	2 21 -25	6 168-183
-4 244-226	-8 34 -48	3 171-155	7 54 38
-3 196-171	-7 51 63	4 72 61	
-2 139 111	-6 195 214		H,K= 4, 5
-1 98 86	-5 0 -5	H,K=12, 4	L FOB FCA
-0 31 -6	-4 205-169	L FOB FCA	-7 135-137
1 331-351	-3 61 -58	-5 104 -89	-6 126 118
2 233-236	-2 45 31	-4 62 -58	-5 0 15
3 77 -79	-1 137 144	-3 165 182	-4 32 25
4 154 156	-0 187 190	-2 24 37	-3 90 63
5 31 12	1 52 -42	-1 82 -81	-2 30 -9
6 95-100	2 229-229	-0 64 57	-1 211-218
7 185-200	3 45 -41	1 22 -15	-0 150 148
8 45 -47	4 102 104	2 75 -71	1 35 33
	5 115 116	3 126 120	2 44 -34
H,K= 2, 4	6 43 46		3 51 52
L FOB FCA	7 48 -58	H,K=13, 4	4 32 28
-8 124 107		L FOB FCA	5 167-175
-7 83 -75	H,K= 7, 4	-4 32 7	6 68 70
-6 104 -94	L FOB FCA	-3 74 76	7 46 57
-5 23 -30	-7 84 86	-2 18 -17	
-4 235-192	-6 173-181	-1 34 -21	H,K= 5, 5
-3 102 76	-5 167-144	-0 0 -18	L FOB FCA
-2 258 235	-4 167 144	1 84 -85	-7 80 -83
-1 106-111	-3 138-140	2 37 34	-6 199 214
-0 237-253	-2 50 -49		-5 107-100
1 64 -64	-1 102 103	H,K=14, 4	-4 114 -94
2 61 -58	-0 147-143	L FOB FCA	-3 241-216
3 100 99	1 246-248	-2 66 -81	-2 167-172
4 164 166	2 123 121	-1 30 -16	-1 90 -92
5 95 -99	3 50 -47	-0 195-187	-0 256 271
6 187-202	4 64 -67		1 153-156
7 26 -26	5 34 34	H,K= 0, 5	2 162-160
8 30 48	6 33 -37	L FOB FCA	3 189-196
		1 164 162	4 35 -40
H,K= 3, 4	H,K= 8, 4	2 78 -70	5 47 -38
L FOB FCA	L FOB FCA	3 122-123	6 118 126
-8 154-148	-7 102-117	4 92 90	
-7 162 158	-6 180-180	5 137 135	H,K= 6, 5
-6 146 125	-5 134 112	6 0 -30	L FOB FCA
-5 59 47	-4 137-124	7 93 88	-7 132 156
-4 23 23	-3 68 -65		-6 76 -87
-3 449 431	-2 29 -19	H,K= 1, 5	-5 34 11
-2 233-221	-1 115-118	L FOB FCA	-4 153-141
-1 160 168	-0 199-206	-7 174 162	-3 113-108
-0 225 236	1 158 154	-6 60 52	-2 38 -36
1 129 126	2 95 -84	-5 98 90	-1 264 288
2 91 -96	3 132-127	-4 218-203	-0 111-109
3 408 426	4 0 -4	-3 220 206	1 101-107
4 83 -85	5 22 -21	-2 361 318	2 128-136
5 25 37	6 136-132	-1 272 261	3 0 2
6 103 103		-0 98 -98	4 0 -1
7 128 134	H,K= 9, 4	1 79 80	5 189 189
	L FOB FCA	2 109-112	6 77 -84
H,K= 4, 4	-7 58 -53	3 247 261	
L FOB FCA	-6 92 -68	4 231 237	H,K= 7, 5
-8 41 -12	-5 193 175	5 140 146	L FOB FCA
-7 27 22	-4 39 34	6 105-113	-7 52 54
-6 25 13	-3 169 185	7 46 51	-6 130 126
-5 32 41	-2 15 -15		-5 95 74
-4 205 189	-1 34 -31	H,K= 2, 5	-4 74 -76
-3 103 -86	-0 41 -43	L FOB FCA	-3 216 226

-2 51 61	H,K= 1, 6	-0 63 70	-1 207-193
-1 39 39	L FOB FCA	1 0 -27	-0 41 -4
-0 113 111	-7 220 206	2 210-224	1 52 -55
1 125 128	-6 150-146	3 128 130	2 121-135
2 94 -98	-5 118-109	4 81 85	3 65 66
3 163 155	-4 35 22	5 0 -12	4 49 31
4 127 121	-3 80 69		5 137-155
5 23 29	-2 47 -16	H,K= 7, 6	6 36 -48
6 0 -1	-1 261 236	L FOB FCA	
	-0 213-217	-6 25 -26	H,K= 2, 7
H,K= 8, 5	1 136-148	-5 48 2	L FOB FCA
L FOB FCA	2 60 57	-4 48 -32	-6 0 -3
-6 36 -12	3 152 165	-3 68 -63	-5 173-153
-5 109 -92	4 62 -57	-2 41 31	-4 182 159
-4 141 133	5 101 100	-1 137 158	-3 136 126
-3 37 30	6 135-136	-0 47 -48	-2 63 56
-2 41 -42	7 49 -50	1 60 -66	-1 123 135
-1 90 93		2 0 -15	-0 41 42
-0 55 55	H,K= 2, 6	3 15 12	1 163-181
1 129-131	L FOB FCA	4 0 4	2 158 179
2 94 101	-7 122 -98	5 110 111	3 169 190
3 70 66	-6 0 2		4 33 5
4 38 -34	-5 75 -67	H,K= 8, 6	5 36 19
5 29 32	-4 51 -48	L FOB FCA	
	-3 85 -65	-6 46 47	H,K= 3, 7
H,K= 9, 5	-2 260 241	-5 84 -82	L FOB FCA
L FOB FCA	-1 155-157	-4 54 36	-6 43 -44
-6 143-130	-0 102-106	-3 40 23	-5 41 23
-5 50 25	1 51 -52	-2 149 161	-4 127 113
-4 208 204	2 48 55	-1 142-153	-3 151 135
-3 45 -27	3 82 -87	-0 29 29	-2 133 124
-2 115-129	4 141 158	1 62 -68	-1 92 -59
-1 36 -36	5 116-123	2 37 27	-0 89 -91
-0 73 -70	6 95-104	3 22 -8	1 74 82
1 47 60		4 137 140	2 175 192
2 139 135	H,K= 3, 6		3 59 70
3 48 -39	L FOB FCA	H,K= 9, 6	4 54 60
4 108-105	-7 53 -40	L FOB FCA	5 73 -85
	-6 108 -98	-5 43 5	
H,K=10, 5	-5 268-246	-4 26 -16	H,K= 4, 7
L FOB FCA	-4 63 66	-3 28 -5	L FOB FCA
-6 108 95	-3 24 -7	-2 159-170	-6 50 -25
-5 220 192	-2 52 -56	-1 202-215	-5 112 102
-4 61 56	-1 118-126	-0 57 50	-4 58 -60
-3 170-187	-0 95 -96	1 34 35	-3 38 40
-2 49 37	1 264-285	2 49 -49	-2 192-190
-1 62 -65	2 76 75	3 55 -53	-1 35 39
-0 106 107	3 65 66	4 110-104	-0 0 -9
1 162 160	4 59 -68		1 103 113
2 30 25	5 175-188	H,K=10, 6	2 74 -80
3 209-203	6 0 -22	L FOB FCA	3 43 48
4 23 22		-5 0 -14	4 129-154
	H,K= 4, 6	-4 43 46	5 0 14
H,K=11, 5	L FOB FCA	-3 62 -62	
L FOB FCA	-7 29 9	-2 206-236	H,K= 5, 7
-5 108-106	-6 62 -54	-1 122 132	L FOB FCA
-4 46 -21	-5 164 163	-0 106 99	-5 53 -83
-3 57 -48	-4 94 82	1 52 -45	-4 0 10
-2 83 -85	-3 56 -44	2 48 -45	-3 0 -2
-1 16 -4	-2 58 -60	3 23 -22	-2 63 -64
-0 75 71	-1 52 56		-1 149 164
1 113-114	-0 82 -78	H,K=11, 6	-0 77 79
2 79 -74	1 174 182	L FOB FCA	1 110-119
3 33 -31	2 103 108	-4 34 13	2 21 -31
	3 42 -49	-3 28 -26	3 49 54
H,K=12, 5	4 73 -76	-2 62 67	4 16 -17
L FOB FCA	5 64 75	-1 74 73	5 60 74
-4 92 -91	6 44 -38	-0 23 22	
-3 58 -52		1 96 99	H,K= 6, 7
-2 40 -40	H,K= 5, 6	2 24 23	L FOB FCA
-1 44 40	L FOB FCA		-5 38 14
-0 179-173	-6 100 106	H,K=12, 6	-4 29 -1
1 52 51	-5 228 229	L FOB FCA	-3 249-245
2 41 -39	-4 90 -78	-2 32 -43	-2 128 139
	-3 150-135	-1 70 78	-1 71 75
H,K=13, 5	-2 184 190	-0 42 41	-0 101-100
L FOB FCA	-1 173 185		1 75 -82
-3 72 80	-0 99 93	H,K= 0, 7	2 50 58
-2 119 127	1 136 139	L FOB FCA	3 158-165
-1 30 -6	2 55 -57	1 74 -83	4 72 75
-0 62 -50	3 81 -85	2 94 -92	
	4 162 170	3 127-125	H,K= 7, 7
H,K= 0, 6	5 139 143	4 93 92	L FOB FCA
L FOB FCA	6 31 31	5 68 -61	-5 146-128
-0 72 67		6 32 -14	-4 211-186
1 139-142	H,K= 6, 6		-3 38 -32
2 122-119	L FOB FCA	H,K= 1, 7	-2 67 66
3 0 19	-6 111 113	L FOB FCA	-1 45 -41
4 109-105	-5 62 -44	-6 68 54	-0 63 -59
5 85 84	-4 248-216	-5 129-124	1 115-124
6 67 59	-3 139 131	-4 181-174	2 168-178
7 92 -93	-2 0 8	-3 104 107	3 16 16
	-1 15 14	-2 40 27	4 92 89

	-3 92 -75
H,K= 8, 7	-2 58 48
L FOB FCA	-1 82 -80
-4 91 76	-0 27 -40
-3 64 60	1 0 -1
-2 67 68	2 67 -68
-1 46 -48	3 62 -64
-0 39 -41	
1 41 -33	H,K= 6, 8
2 99 104	L FOB FCA
3 64 60	-4 0 30
	-3 45 44
H,K= 9, 7	-2 28 38
L FOB FCA	-1 48 55
-4 94 96	-0 234 231
-3 36 -44	1 132-149
-2 32 -33	2 0 -7
-1 65 71	3 73 79
-0 33 38	
1 123 125	H,K= 7, 8
2 66 65	L FOB FCA
	-3 68 60
H,K=10, 7	-2 86 93
L FOB FCA	-1 151 164
-3 30 33	-0 117-118
-2 26 -7	1 83 -90
-1 39 -23	2 52 58
-0 0 19	
1 144 152	H,K= 8, 8
	L FOB FCA
H,K= 0, 8	-2 19 -26
L FOB FCA	-1 31 6
-0 161 160	-0 125-119
1 36 -15	1 41 55
2 124 121	
3 27 -8	H,K= 0, 9
4 98 104	L FOB FCA
5 0 21	1 59 45
	2 40 6
H,K= 1, 8	3 81 -85
L FOB FCA	
-5 51 26	H,K= 1, 9
-4 63 44	L FOB FCA
-3 97 -88	-3 85 75
-2 98 89	-2 0 1
-1 117 106	-1 0 7
-0 81 -83	-0 49 49
1 0 -7	1 55 -60
2 79 86	2 89 -97
3 66 -64	3 63 55
4 46 22	
	H,K= 2, 9
H,K= 2, 8	L FOB FCA
L FOB FCA	-3 44 20
-5 30 7	-2 91 -92
-4 193-167	-1 46 26
-3 212 192	-0 252-260
-2 125 115	1 69 -71
-1 114-116	2 76 79
-0 162-169	
1 87 98	H,K= 3, 9
2 102-113	L FOB FCA
3 114 129	-2 0 22
4 74 79	-1 113-121
	-0 44 -48
H,K= 3, 8	1 91 100
L FOB FCA	2 86 96
-5 44 -7	
-4 111 101	H,K= 4, 9
-3 141 130	L FOB FCA
-2 83 -66	-2 114 117
-1 117-122	-1 67 -78
-0 0 -2	-0 95 95
1 15 31	1 70 81
2 105 119	
3 90 100	H,K= 5, 9
4 93-109	L FOB FCA
	-1 52 61
H,K= 4, 8	-0 48 47
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	

3.202 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.

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°

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

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 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.

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.

References

(1) Work done under the auspices of the U. S. Atomic Energy Commission.

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Figure Captions

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).

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

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

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.

ThI_4

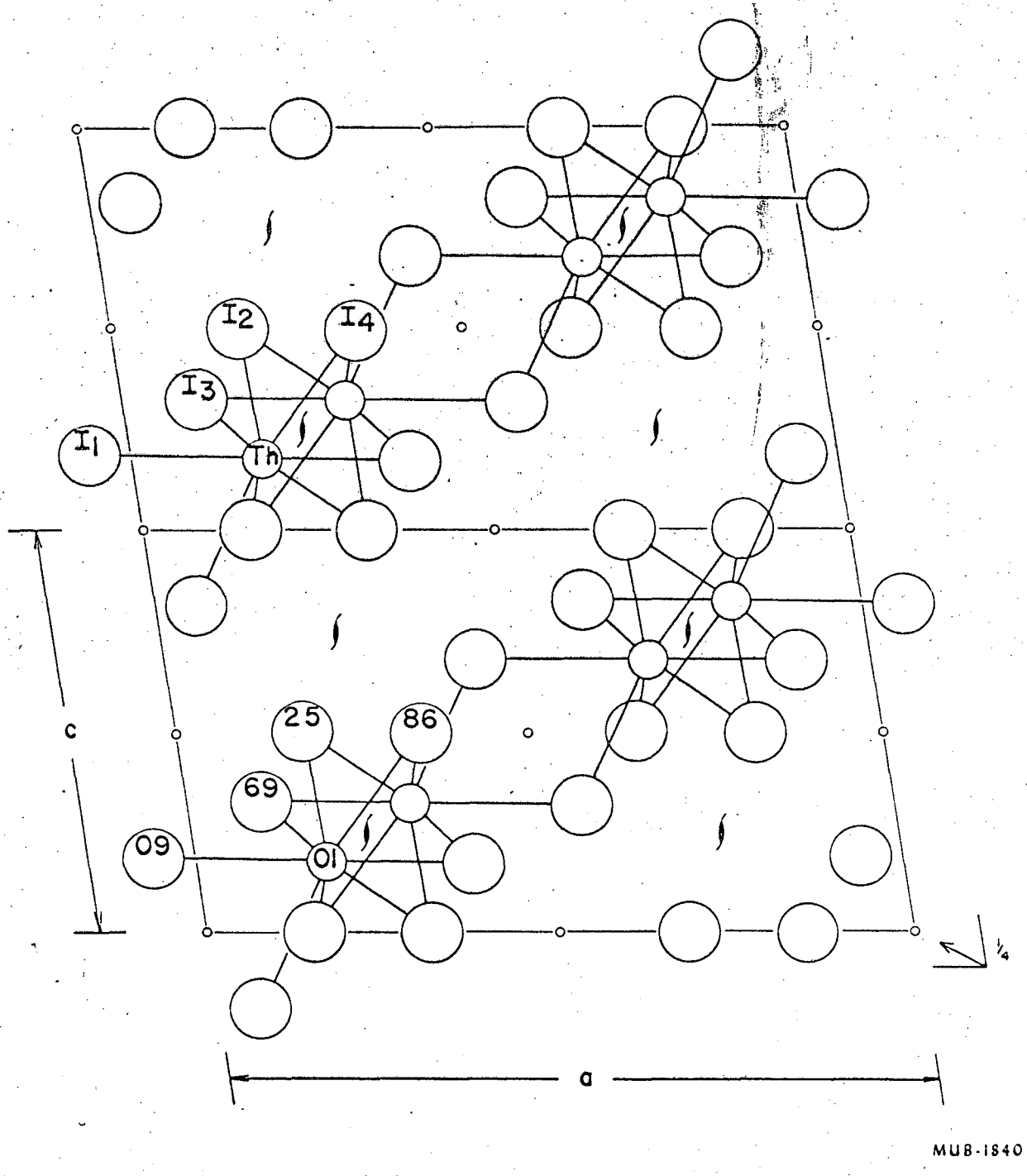
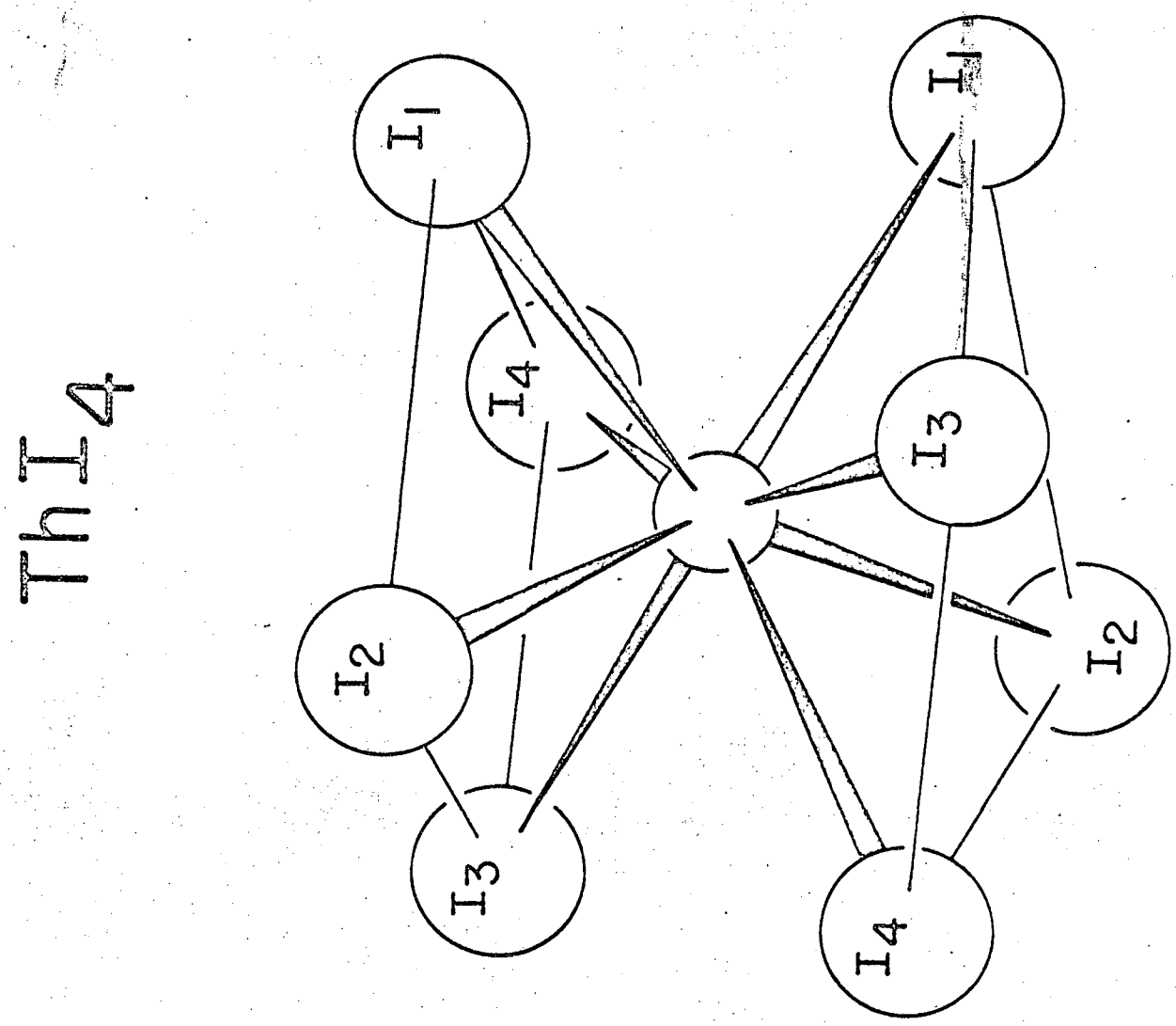


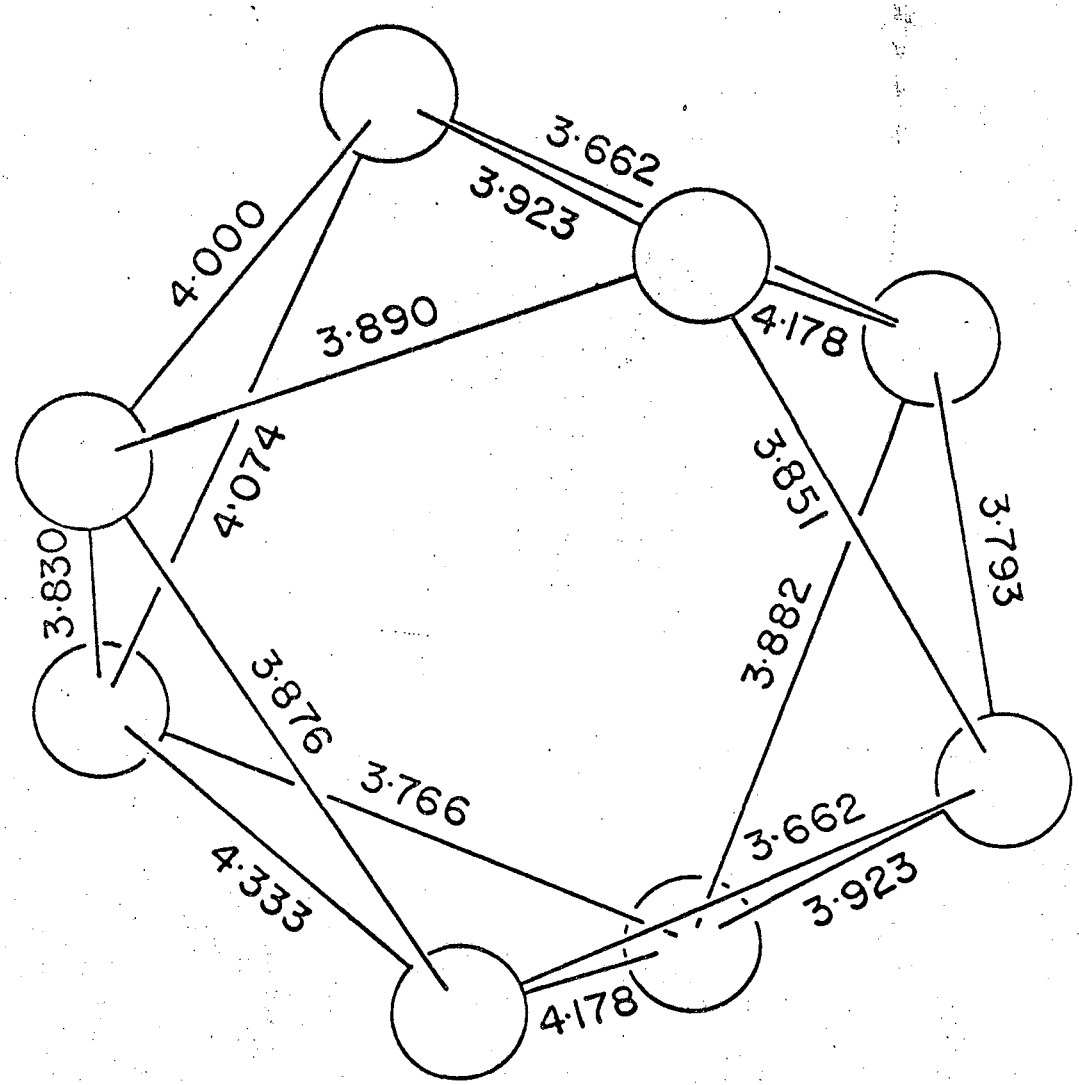
Fig. 1



MU-30571

Fig. 2

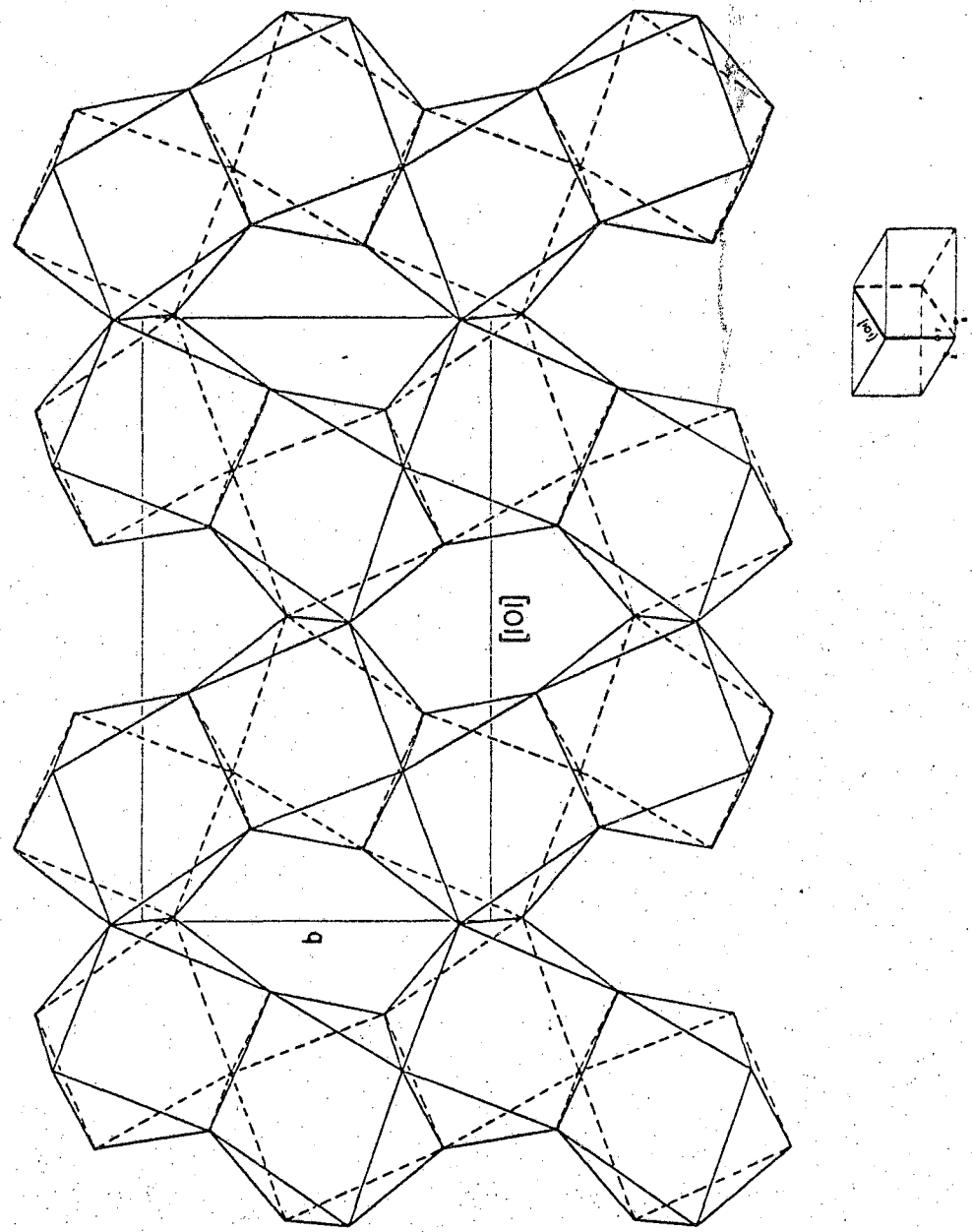
ThI_4



MU-30570

Fig. 3

ThI_4



MUB-1841

Fig. 4

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