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Berkeley, California

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CRYSTAL STRUCTURE OF THORIUM NITRATE PENTAHYDRATE BY X-RAY DIFFRACTION

Tatzuo Ueki, Allan Zalkin and David H. Templeton

October 1965

Crystal Structure of Thorium Nitrate Pentahydrate by X-ray Diffraction*

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Crystals of $Th(NO_3)_4 \cdot 5H_2O$ are orthorhombic, space group Fdd2, $a = 11.182$, $b = 22.873$, $c = 10.573$ Å, $Z = 8$. Thorium has three water molecules and 8 oxygen atoms from four nitrate ions as neighbors in a highly polar arrangement. All hydrogen atoms are in hydrogen bonds 2.71 to 2.96 Å in length. Average bond distances are: Th-O (water) = 2.46 Å, Th-O (nitrate) = 2.57 Å, N-O (next to Th) = 1.27 Å, N-O (terminal) = 1.22 Å. An error of about 0.05 Å is made in the position of the thorium atom if anomalous dispersion ($\Delta f'' = 9$) is neglected.

Thorium nitrate crystallizes readily from aqueous nitric acid solutions as the pentahydrate, $Th(NO_3)_4 \cdot 5H_2O$. The earlier literature is confused and contradictory concerning its composition, and it is often found in chemical store rooms labeled as $Th(NO_3)_4 \cdot 4H_2O$. Ferraro, Katzin & Gibson (1954) made a definitive study of the phase diagram and showed that the tetrahydrate crystallizes only when the nitric acid concentration is very high.

*Work done under the auspices of the U. S. Atomic Energy Commission.

An earlier X-ray study of the pentahydrate, then referred to as the hexahydrate, revealed the unit cell, space group, and thorium atom positions (Templeton & Dauben, 1950). No attempt was made at that time to determine the rest of the structure. With the advantage of electronic computers and better methods for X-ray intensity measurement, we recently solved the structure as reported in the present paper. An independent analysis by neutron diffraction, with results in good agreement with ours, is described in the adjacent paper (Taylor, Mueller & Hitterman, 196x). These studies confirm the composition, show an interesting coordination geometry for the thorium ions, and reveal an intricate structure of hydrogen bonds.

Experimental

A bottle from Allied Chemical, General Chemical Division, New York, and labeled $Th(NO_3)_4 \cdot 4H_2O$ contained large clear colorless crystals and white powder. Our X-ray diffraction data were obtained from a fragment with dimensions 0.22 × 0.08 × 0.08 mm which was cut from one of the clear crystals. It was sealed in a silica-glass capillary (wall thickness 0.01 mm) to prevent deliquescence. Cell dimensions and intensities were measured with the General Electric XRD-5 goniostat with scintillation counter and pulse-height discriminator, using molybdenum radiation. Cell dimensions are based on $\lambda(K\alpha_1) = 0.70926$ Å. Intensities were measured of 1036 independent reflections (121 recorded as zero) with the stationary crystal technique and counting time of 10 sec. A search for violations of the space-group rules failed to detect any. The thorium atoms in the special positions 8(a) cause intensities to be weak if $\underline{h} + \underline{k} + \underline{\ell} = 4\underline{n} + 2$, especially at large diffraction angles. For fear that many weak or zero data would be undesirable in the least-squares calculations, we assigned zero weight to the 156 reflections

with 2θ greater than 40° and with counting rates of 2 counts/sec or less. No correction was made for absorption or extinction. We estimate the absorption parameter $\mu\underline{R}$ as 1.3 for the smaller dimensions of the crystal, and this effect limits the accuracy of the thermal parameters.

Calculations were made with the IBM 7044 computer using an unpublished full-matrix least-squares program which minimized $\Sigma \underline{w}(|\underline{F}_o| - |\underline{F}_c|)^2 / \Sigma \underline{w}|\underline{F}_o|^2$. The weights $\underline{w}$ were taken as unity or zero. Atomic scattering factors for Th^{4+} were obtained by extrapolation from the values for Yb^{4+} and Hg^{4+} (Thomas & Umeda, 1957) with corrections $\Delta\underline{f}' = -6$ and $\Delta\underline{f}'' = 9$ for anomalous dispersion. For nitrogen and oxygen we used form factors for neutral atoms as listed by Ibers (1962).

Unit cell and space group

$Th(NO_3)_4 \cdot 5H_2O$ crystals are orthorhombic, space group Fdd2, with 8 formula units in the cell:

$\underline{a}$ = 11.182 ± 0.003 Å (11.191 ± 0.005 Å),

$\underline{b}$ = 22.873 ± 0.005 Å (22.889 ± 0.010 Å),

$\underline{c}$ = 10.573 ± 0.003 Å (10.579 ± 0.005 Å).

The dimensions found by Taylor, Mueller & Hitterman (196x) are given in parentheses. The discrepancy of 6 to 8 parts in 10,000 is only slightly more than one would expect from the estimated accuracies. The density calculated from our data, 2.800 ± 0.002 g cm^{-3}, is between the density measured by flotation in this laboratory, 2.84, and that reported by Staritzky (1956), 2.787. Our measurements were made at about 21°C.

Crystal data for the isomorphous cerium and plutonium compounds are given by Staritzky (1956). These crystals are expected to have very nearly the same atomic arrangement.

Determination of the structure

The thorium atoms are in the special position set 8(a): (0, 0, z; 1/4, 1/4, 1/4 + z) + F, and for this first atom z can be taken as zero. Refinement of the two parameters (scale factor and isotropic thermal parameter) reduced $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ to 0.147. This partial structure has symmetry Fddd, and therefore a Fourier calculation phased by the thorium atom shows duplicate images of the rest of the structure. Furthermore, no phase information is obtained for reflections with $h + k + \ell = 4n + 2$, which constitute about one-fourth of the data. The structure was solved by selecting various peaks in the Fourier functions as trial atoms and testing the behavior of their thermal parameters in least-squares calculations. At the third round of this, the nitrate groups were recognized. After several more trials, R was reduced to 0.077 (isotropic thermal parameters) or 0.062 (thorium atom anisotropic) with one water molecule not correctly placed. The correct structure gave $R = 0.043$, with only the thorium atom anisotropic. Further refinement with anisotropic thermal parameters for all atoms (hydrogen excluded) reduced R to 0.034.

We had proceded with the assumption that the water content was in doubt. To check for additional water molecules, we calculated a Fourier synthesis of $(F_o - F_c)$, deleting reflections with zero intensity. The largest peaks in this function were about 0.28 electron $Å^{-3}$, in the neighborhood of the thorium atom. No evidence was found of further water molecules. With the help of an assignment of hydrogen bonds five peaks about one-third to one-half as high as the largest were selected as hydrogen atoms (Table 1). No attempt was made to include hydrogen in any of the structure factor calculations, or to refine these positions.

Table 1. Approximate hydrogen coordinates

x	y	z
0.45	-0.04	-0.25
0.33	-0.14	-0.16
0.06	0.12	0.06
0.35	0.18	-0.26
0.30	-0.14	0.16

Table 2. Structure factor magnitudes, observed (FOB) and calculated (FCA)

An asterisk (*) indicates zero weight.

(Table to be reproduced photographically)

H,K= 0, 0
L FOB FCA
4 660 668
8 263 256
12 191 193

H,K= 0, 2
L FOB FCA
10 241 249
14 134 124

H,K= 0, 4
L FOB FCA
0 699 712
4 661 669
8 318 331
12 167 167

H,K= 0, 6
L FOB FCA
2 800 806
6 374 391
10 198 206
14 130 128

H,K= 0, 8
L FOB FCA
0 522 510
4 504 523
8 260 263
12 140 146

H,K= 0,10
L FOB FCA
2 586 581
6 317 327
10 178 176
14 98 103

H,K= 0,12
L FOB FCA
0 539 535
4 415 416
8 280 274
12 128 122

H,K= 0,14
L FOB FCA
2 309 309
6 283 274
10 165 169

H,K= 0,16
L FOB FCA
0 447 430
4 386 387
8 182 183
12 113 117

H,K= 0,18
L FOB FCA
2 355 343
6 285 285
10 159 147

H,K= 0,20
L FOB FCA
0 418 424
4 261 259
8 171 160

H,K= 0,22
L FOB FCA
2 317 327
6 202 196
10 145 143

H,K= 0,24
L FOB FCA
0 275 271
4 240 246
8 192 195

H,K= 0,26
L FOB FCA
2 228 240
6 151 165

H,K= 0,28
L FOB FCA
0 213 233
4 215 215

H,K= 0,30
L FOB FCA
2 175 178

H,K= 0,32
L FOB FCA
0 148 153

H,K= 1, 1
L FOB FCA
1 471 461
3 352 351
5 427 441
7 242 252
9 201 207
11 135 139
13 117 120

H,K= 1, 3
L FOB FCA
1 450 444
3 346 356
5 338 348
7 227 234
9 234 233
11 174 171
13 102 111

H,K= 1, 5
L FOB FCA
1 415 403
3 353 341
5 346 355
7 307 314
9 198 201
11 159 155
13 103 100

H,K= 1, 7
L FOB FCA
1 372 355
3 435 436
5 199 213
7 271 280
9 220 225
11 139 140
13 92 99

H,K= 1, 9
L FOB FCA
1 344 334
3 415 408
5 274 278
7 214 218
9 193 196
11 126 120
13 99 106

H,K= 1,11
L FOB FCA
1 267 264
3 371 375
5 256 267
7 196 196
9 156 163
11 107 110
13 101 103

H,K= 1,13
L FOB FCA
1 260 264
3 210 211
5 314 317
7 176 179
9 191 188
11 114 121
13 73 91

H,K= 1,15
L FOB FCA
1 264 255
3 189 189
5 281 273
7 217 222
9 160 152
11 117 119
13 74 82

H,K= 1,17
L FOB FCA
1 288 285
3 211 200
5 216 209
7 134 142
9 153 156
11 110 109

H,K= 1,19
L FOB FCA
1 269 264
3 212 210
5 184 181
7 161 176
9 128 122
11 101 99

H,K= 1,21
L FOB FCA
1 201 201
3 216 206
5 203 200
7 135 135
9 124 116
11 98 92

H,K= 1,23
L FOB FCA
1 200 190
3 186 185
5 141 145
7 133 136
9 113 110

H,K= 1,25
L FOB FCA
1 171 162
3 149 141
5 159 159
7 135 125
9 111 106

H,K= 1,27
L FOB FCA
1 136 154
3 164 167
5 115 110
7 89 104

H,K= 1,29
L FOB FCA
1 130 142
3 106 109
5 103 117

H,K= 1,31
L FOB FCA
1 103 114
3 111 111

H,K= 2, 0
L FOB FCA
2 281 274
6 373 375
10 263 248
14 119 118

H,K= 2, 2
L FOB FCA
0 604 593
2 91 88
4 480 492
6 30 34
8 317 318
10 0 22
12 168 168
14 0 11*

H,K= 2, 4
L FOB FCA
0 165 147
2 361 387
4 109 115
6 410 414
8 0 25
10 246 246
12 0 20*
14 125 130

H,K= 2, 6
L FOB FCA
0 240 243
2 57 50
4 488 497
6 45 43
8 344 343
10 0 19*
12 185 179
14 0 3*

H,K= 2, 8
L FOB FCA
0 125 121
2 576 572
4 67 63
6 360 373
8 46 52
10 234 233
12 0 2*
14 127 122

H,K= 2,10
L FOB FCA
0 719 705
2 65 63
4 389 393
6 34 33
8 300 300
10 0 17*
12 200 183
14 0 7*

H,K= 2,12
L FOB FCA
0 20 26
2 438 421
4 79 73
6 313 304
8 40 28
10 245 239
12 34 4*

H,K= 2,14
L FOB FCA
0 455 454
2 60 47
4 412 417
6 46 24
8 300 300
10 0 21*
12 141 150

H,K= 2,16
L FOB FCA
0 71 65
2 314 312
4 51 46
6 309 317
8 43 44*
10 201 205
12 0 7*

H,K= 2,18
L FOB FCA
0 360 353
2 37 22
4 327 325
6 0 13*
8 196 197
10 0 3*
12 133 130

H,K= 2,20
L FOB FCA
0 38 30
2 303 293
4 41 41
6 250 246
8 0 22*
10 149 152

H,K= 2,22
L FOB FCA
0 227 229
2 29 11*
4 226 225
6 55 34
8 201 200
10 0 2*

H,K= 2,24
L FOB FCA
0 31 4*
2 205 191
4 0 21*
6 176 178
8 0 15*

H,K= 2,26
L FOB FCA
0 193 190
2 0 28*
4 206 198
6 0 17*
8 156 144

H,K= 2,28
L FOB FCA
0 0 3*
2 168 164
4 0 4*
6 146 141

H,K= 2,30
L FOB FCA
0 182 175
2 0 25*
4 147 146

H,K= 3, 1
L FOB FCA
1 418 424
3 442 443
5 351 348
7 162 161
9 182 179
11 127 121
13 109 102

H,K= 3, 3
L FOB FCA
1 347 347
3 336 341
5 326 333
7 245 252
9 187 181
11 102 104
13 98 91

H,K= 3, 5
L FOB FCA
1 412 421
3 310 316
5 310 313
7 267 270
9 203 200
11 156 147
13 98 98

H,K= 3, 7
L FOB FCA
1 481 484
3 395 402
5 268 266
7 207 207
9 166 167
11 138 137
13 93 98

H,K= 3, 9
L FOB FCA
1 517 510
3 322 326
5 275 279
7 219 212
9 147 147
11 101 114
13 87 107

H,K= 3,11
L FOB FCA
1 400 400
3 358 352
5 301 307
7 211 213
9 175 177
11 131 134
13 65 98

H,K= 3,13
L FOB FCA
1 365 355
3 313 318
5 289 277
7 161 161
9 164 162
11 125 120
13 90 92

H,K= 3,15
L FOB FCA
1 332 327
3 209 208
5 224 229
7 188 182
9 169 156
11 109 116

H,K= 3,17
L FOB FCA
1 264 254
3 273 265
5 228 221
7 179 182
9 165 164
11 86 95

H,K= 3,19
L FOB FCA
1 255 249
3 249 238
5 191 199
7 136 132
9 111 116
11 81 90

H,K= 3,21
L FOB FCA
1 199 188
3 187 181
5 159 153
7 134 131
9 104 111

H,K= 3,23
L FOB FCA
1 159 162
3 171 168
5 167 174
7 140 139
9 95 97

H,K= 3,25
L FOB FCA
1 135 132
3 134 135
5 143 138
7 100 110

H,K= 3,27
L FOB FCA
1 130 133
3 113 111
5 117 109
7 90 96

H,K= 3,29
L FOB FCA
1 153 153
3 113 114
5 97 112

H,K= 3,31
L FOB FCA
1 104 104

H,K= 4, 0
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0 683 702
4 533 536
8 337 321
12 155 159

H,K= 4, 2
L FOB FCA
0 127 118
2 540 558
4 144 133
6 340 339
8 64 62
10 252 240
12 0 11*
14 116 122

H,K= 4, 4
L FOB FCA
0 460 480
2 60 50
4 494 504
6 52 56
8 322 317
10 0 20*
12 166 162
14 0 9*

H,K= 4, 6
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2 398 423
4 107 107
6 397 412
8 71 57
10 215 215
12 0 4*
14 117 112

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2 90 84
4 390 402
6 42 50
8 254 259
10 31 31*
12 148 157

H,K= 4,10
L FOB FCA
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2 405 400
4 33 37
6 322 319
8 0 30
10 179 177
12 0 4*

H,K= 4,12
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4 347 352
6 46 41
8 253 243
10 0 20*
12 132 135

H,K= 4,14
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4 72 57
6 283 279
8 0 14*
10 171 181
12 0 12*

H,K= 4,16
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2 26 9
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6 57 66
8 217 209
10 0 6*
12 110 116

H,K= 4,18
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2 345 340
4 28 21
6 216 213
8 46 22*
10 144 148

H,K= 4,20
L FOB FCA
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2 64 63
4 260 263
6 31 21*
8 174 174
10 0 17*

H,K= 4,22
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2 274 258
4 44 37*
6 196 193
8 0 10*
10 134 133

H,K= 4,24
L FOB FCA
0 268 258
2 0 15*
4 221 216
6 0 14*
8 173 163

H,K= 4,26
L FOB FCA
0 0 12*
2 213 200
4 0 15*
6 174 174

H,K= 4,28
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2 35 25*
4 196 183
6 0 13*

H,K= 4,30
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0 0 25*
2 179 170

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3 394 394
5 268 271
7 209 207
9 193 190
11 131 138
13 100 106

H,K= 5, 3
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3 414 411
5 325 318
7 223 225
9 218 210
11 157 153
13 100 104

H,K= 5, 5
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1 403 407
3 301 316
5 246 243
7 201 205
9 186 184
11 125 124
13 94 102

H,K= 5, 7
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3 232 227
5 308 304
7 256 256
9 179 172
11 108 112
13 72 87

H,K= 5, 9
L FOB FCA
1 304 319
3 282 288
5 303 298
7 180 177
9 147 149
11 133 124
13 89 87

H,K= 5,11
L FOB FCA
1 317 315
3 212 216
5 214 218
7 140 144
9 119 115
11 101 107
13 83 89

H,K= 5,13
L FOB FCA
1 161 161
3 204 205
5 241 235
7 224 216
9 161 152
11 60 86

H,K= 5,15
L FOB FCA
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3 254 244
5 217 207
7 161 154
9 152 144
11 106 100

H,K= 5,17
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3 193 200
5 159 159
7 120 130
9 116 123
11 81 92

H,K= 5,19
L FOB FCA
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3 183 176
5 163 168
7 125 138
9 109 117
11 74 88

H,K= 5,21
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3 204 211
5 155 159
7 121 117
9 101 112

H,K= 5,23
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3 146 144
5 141 145
7 110 122
9 117 114

H,K= 5,25
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3 142 138
5 138 134
7 120 117

H,K= 5,27
L FOB FCA
1 158 157
3 140 138
5 120 133

H,K= 5,29
L FOB FCA
1 108 108
3 116 107

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6 285 283
10 201 201

H,K= 6, 2
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2 42 43
4 383 386
6 79 72
8 295 286
10 31 35*
12 161 163

H,K= 6, 4
L FOB FCA
0 0 1
2 335 333
4 73 65
6 345 354
8 0 29
10 232 228
12 0 6*

H,K= 6, 6
L FOB FCA
0 445 445
2 110 107
4 389 384
6 118 105
8 278 269
10 0 17*
12 156 155

H,K= 6, 8
L FOB FCA
0 94 98
2 365 362
4 42 43
6 296 290
8 29 48*
10 208 201
12 0 8*

H,K= 6,10
L FOB FCA
0 396 388
2 41 36
4 379 373
6 0 15
8 251 244
10 0 13*
12 129 133

H,K= 6,12
L FOB FCA
0 81 79
2 328 318
4 37 44
6 282 284
8 0 25*
10 189 183
12 0 7*

H,K= 6,14
L FOB FCA
0 304 299
2 90 82
4 306 304
6 29 24*
8 229 231
10 0 6*
12 128 134

H,K= 6,16
L FOB FCA
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2 288 285
4 28 46
6 260 253
8 0 21*
10 164 158

H,K= 6,18
L FOB FCA
0 296 294
2 41 25
4 269 258
6 31 17*
8 198 195
10 0 6*

H,K= 6,20
L FOB FCA
0 0 22*
2 259 250
4 31 49*
6 190 187
8 0 8*
10 139 140

H,K= 6,22
L FOB FCA
0 248 254
2 45 61*
4 211 218
6 34 16*
8 156 154

H,K= 6,24
L FOB FCA
0 0 14*
2 169 172
4 0 5*
6 173 178
8 0 7*

H,K= 6,26
L FOB FCA
0 182 186
2 35 10*
4 177 168
6 0 18*

H,K= 6,28
L FOB FCA
0 0 33*
2 166 168
4 0 21*

H,K= 7, 1
L FOB FCA
1 277 281
3 251 246
5 256 245
7 217 200
9 142 136
11 121 118
13 82 83

H,K= 7, 3
L FOB FCA
1 264 266
3 205 210
5 205 209
7 211 214
9 146 138
11 106 96
13 82 88

H,K= 7, 5
L FOB FCA
1 187 183
3 294 284
5 284 275
7 190 190
9 200 186
11 117 104
13 83 80

H,K= 7, 7
L FOB FCA
1 292 292
3 263 264
5 259 254
7 166 162
9 165 155
11 119 120

H,K= 7, 9
L FOB FCA
1 334 328
3 242 226
5 231 229
7 140 148
9 159 153
11 115 110

H,K= 7,11
L FOB FCA
1 297 298
3 273 271
5 213 210
7 181 186
9 145 151
11 112 112

H,K= 7,13
L FOB FCA
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3 249 250
5 204 200
7 162 159
9 152 148
11 108 108

H,K= 7,15
L FOB FCA
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3 225 224
5 171 168
7 185 184
9 140 138
11 82 88

H,K= 7,17
L FOB FCA
1 223 227
3 193 183
5 209 204
7 150 155
9 111 110

H,K= 7,19
L FOB FCA
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3 179 188
5 170 165
7 107 124
9 72 93

H,K= 7,21
L FOB FCA
1 173 159
3 116 110
5 160 154
7 116 113
9 98 97

H,K= 7,23
L FOB FCA
1 144 147
3 134 141
5 125 126
7 109 107

H,K= 7,25
L FOB FCA
1 97 103
3 105 119
5 120 123

H,K= 7,27
L FOB FCA
1 102 114
3 97 100

H,K= 8, 0
L FOB FCA
0 374 381
4 370 370
8 210 207
12 119 125

H,K= 8, 2
L FOB FCA
0 53 40
2 414 417
4 0 5
6 313 301
8 0 33*
10 147 140
12 0 4*

H,K= 8, 4
L FOB FCA
0 469 466
2 49 51
4 354 340
6 0 20
8 219 215
10 0 2*
12 120 127

H,K= 8, 6
L FOB FCA
0 43 37
2 343 343
4 53 40
6 271 263
8 31 8*
10 186 179
12 0 5*

H,K= 8, 8
L FOB FCA
0 472 473
2 51 42
4 381 378
6 41 42*
8 214 201
10 34 10*
12 122 113

H,K= 8,10
L FOB FCA
0 26 10
2 423 417
4 39 25
6 200 204
8 0 2*
10 165 162

H,K= 8,12
L FOB FCA
0 370 364
2 39 21
4 310 308
6 0 2*
8 178 183
10 0 6*

H,K= 8,14
L FOB FCA
0 40 38
2 333 331
4 0 7*
6 246 244
8 0 13*
10 143 142

H,K= 8,16
L FOB FCA
0 311 311
2 0 15*
4 243 231
6 46 27*
8 191 185
10 0 10*

H,K= 8,18
L FOB FCA
0 0 2*
2 263 264
4 45 10*
6 185 185
8 0 13*

H,K= 8,20
L FOB FCA
0 270 268
2 0 16*
4 226 231
6 0 4*
8 136 135

H,K= 8,22
L FOB FCA
0 47 23*
2 171 170
4 0 15*
6 164 173

H,K= 8,24
L FOB FCA
0 169 182
2 0 6*
4 178 177
6 0 15*

H,K= 8,26
L FOB FCA
0 0 17*
2 154 163
4 0 5*

H,K= 9, 1
L FOB FCA
1 277 268
3 241 230
5 181 180
7 208 194
9 142 143
11 118 114

H,K= 9, 3
L FOB FCA
1 252 237
3 235 222
5 221 213
7 196 190
9 154 152
11 133 122

H,K= 9, 5
L FOB FCA
1 152 145
3 217 214
5 253 247
7 178 173
9 175 169
11 108 99

H,K= 9, 7
L FOB FCA
1 221 223
3 182 175
5 200 200
7 164 153
9 138 133
11 109 103

H,K= 9, 9
L FOB FCA
1 217 214
3 186 185
5 211 209
7 134 128
9 144 137
11 110 106

H,K= 9,11
L FOB FCA
1 182 176
3 173 165
5 160 158
7 158 156
9 124 127
11 91 94

H,K= 9,13
L FOB FCA
1 190 185
3 163 153
5 139 130
7 136 138
9 111 120

H,K= 9,15
L FOB FCA
1 124 125
3 202 200
5 147 139
7 151 145
9 108 115

H,K= 9,17
L FOB FCA
1 156 152
3 127 127
5 169 155
7 130 124
9 83 91

H,K= 9,19
L FOB FCA
1 79 160
3 74 144
5 76 117
7 62 108

H,K= 9,21
L FOB FCA
1 151 151
3 128 120
5 137 140
7 104 98

H,K= 9,23
L FOB FCA
1 121 126
3 107 114
5 110 105

H,K= 9,25
L FOB FCA
1 109 111
3 98 102

H,K=10, 0
L FOB FCA
2 392 401
6 230 232
10 169 164

H,K=10, 2
L FOB FCA
0 300 301
2 39 57
4 300 289
6 0 11*
8 224 218
10 0 12*

H,K=10, 4
L FOB FCA
0 39 14
2 280 273
4 29 33*
6 255 249
8 0 12*
10 170 174

H,K=10, 6
L FOB FCA
0 345 347
2 57 53
4 271 268
6 31 21*
8 213 215
10 0 5*

H,K=10, 8
L FOB FCA
0 40 19
2 231 223
4 30 24*
6 229 228
8 0 17*
10 149 152

H,K=10,10
L FOB FCA
0 264 259
2 0 14*
4 264 264
6 0 17*
8 160 160
10 0 3*

H,K=10,12
L FOB FCA
0 67 71
2 229 223
4 0 30*
6 227 224
8 0 24*
10 123 127

H,K=10,14
L FOB FCA
0 177 174
2 31 11*
4 206 203
6 0 19*
8 171 169

H,K=10,16
L FOB FCA
0 32 5*
2 214 215
4 0 29*
6 176 170
8 0 9*

H,K=10,18
L FOB FCA
0 204 221
2 0 14*
4 187 190
6 0 21*

H,K=10,20
L FOB FCA
0 0 8*
2 189 190
4 35 6*
6 137 136

H,K=10,22
L FOB FCA
0 191 198
2 0 27*
4 167 176

H,K=10,24
L FOB FCA
0 0 5*
2 143 150

H,K=11, 1
L FOB FCA
1 256 250
3 236 229
5 139 140
7 144 133
9 111 108

H,K=11, 3
L FOB FCA
1 212 217
3 209 198
5 162 161
7 140 132
9 122 110

H,K=11, 5
L FOB FCA
1 208 208
3 215 214
5 169 173
7 125 115
9 112 105

H,K=11, 7
L FOB FCA
1 214 204
3 165 158
5 219 214
7 147 133
9 102 97

H,K=11, 9
L FOB FCA
1 224 218
3 179 176
5 162 162
7 123 121
9 89 95

H,K=11,11
L FOB FCA
1 235 229
3 177 167
5 155 149
7 98 110
9 90 87

H,K=11,13
L FOB FCA
1 172 166
3 146 160
5 162 153
7 128 139

H,K=11,15
L FOB FCA
1 161 157
3 174 171
5 143 138
7 115 109

H,K=11,17
L FOB FCA
1 155 161
3 158 160
5 123 122
7 105 100

H,K=11,19
L FOB FCA
1 131 145
3 147 152
5 103 118

H,K=11,21
L FOB FCA
1 135 143
3 116 120

H,K=11,23
L FOB FCA
1 124 116

H,K=12, 0
L FOB FCA
0 176 177
4 230 226
8 142 146

H,K=12, 2
L FOB FCA
0 31 11*
2 237 232
4 32 17*
6 193 187
8 0 9*

H,K=12, 4
L FOB FCA
0 219 217
2 31 9*
4 223 211
6 34 13*
8 182 180

H,K=12, 6
L FOB FCA
0 44 35*
2 197 195
4 0 9*
6 195 186
8 0 12*

H,K=12, 8
L FOB FCA
0 284 289
2 32 22*
4 224 216
6 0 9*
8 145 152

H,K=12,10
L FOB FCA
0 32 9*
2 231 225
4 0 3*
6 185 192
8 0 10*

H,K=12,12
L FOB FCA
0 229 222
2 0 13*
4 191 200
6 0 9*

H,K=12,14
L FOB FCA
0 34 1*
2 205 213
4 0 10*
6 178 174

H,K=12,16
L FOB FCA
0 194 190
2 0 7*
4 168 177
6 0 20*

H,K=12,18
L FOB FCA
0 36 14*
2 173 177
4 0 7*

H,K=12,20
L FOB FCA
0 173 169
2 0 9*

H,K=13, 1
L FOB FCA
1 163 160
3 169 161
5 119 124
7 119 116

H,K=13, 3
L FOB FCA
1 150 145
3 124 134
5 158 155
7 125 122

H,K=13, 5
L FOB FCA
1 136 142
3 138 147
5 143 141
7 120 115

H,K=13, 7
L FOB FCA
1 149 151
3 152 142
5 131 142
7 104 104

H,K=13, 9
L FOB FCA
1 159 162
3 138 146
5 118 110
7 98 105

H,K=13,11
L FOB FCA
1 150 158
3 126 124
5 114 119

H,K=13,13
L FOB FCA
1 131 135
3 138 128
5 104 110

H,K=13,15
L FOB FCA
1 119 123
3 96 105

H,K=13,17
L FOB FCA
1 97 108
3 112 112

H,K=14, 0
L FOB FCA
2 201 209
6 172 183

H,K=14, 2
L FOB FCA
0 209 226
2 35 2*
4 187 191
6 0 12*

H,K=14, 4
L FOB FCA
0 34 23*
2 181 190
4 50 21*
6 156 160

H,K=14, 6
L FOB FCA
0 184 190
2 0 7*
4 172 180
6 0 7*

H,K=14, 8
L FOB FCA
0 35 15*
2 170 187
4 0 9*

H,K=14,10
L FOB FCA
0 178 173
2 0 6*
4 151 161

H,K=14,12
L FOB FCA
0 0 2*
2 164 166
4 0 4*

H,K=14,14
L FOB FCA
0 139 143
2 0 13*

H,K=15, 1
L FOB FCA
1 140 149
3 110 111

H,K=15, 3
L FOB FCA
1 135 129
3 104 121

H,K=15, 5
L FOB FCA
1 115 119
3 98 113

H,K=15, 7
L FOB FCA
1 110 115
3 118 119

H,K=15, 9
L FOB FCA
1 98 106

The calculations to this point had neglected the out-of-phase component $\Delta f''$ of thorium. Because of the polar nature of the space group Fdd2, two orientations of the structure must be considered, one of which is the reflection of the other in (001). Further calculations with $\Delta f''$ included and the correct orientation reduced R to 0.033 (or 0.045 including reflections of zero weight). With the reverse structure R could not be reduced below 0.035, and the weighted sum of squares was 15 percent larger. In the final cycle of the correct structure, no coordinate shifted more than 0.000008 and no thermal parameter more than 0.001. Observed and calculated structure factor magnitudes are listed in Table 2. The final coordinates are given in Table 3. The anisotropic thermal parameters, Table 4, are listed in the units of the isotropic Debye B, Zalkin, Forrester & Templeton (1964), Cruickshank (1965).

Effect of anomalous dispersion

Inclusion of the thorium phase shift in the calculations gives enough change in some of the structure factor magnitudes to establish the polarity of the structure, but the change in R is hardly dramatic. However, it causes a significant change in the structure. With the origin defined by the thorium atom, all other atoms shifted about 0.05 Å in the positive z direction when the correction was included. A similar shift of the reverse structure causes the two structures, after refinement, to differ by about 0.10 Å. This behavior is explained by the fact that all the calculations were made with reflections with positive values of ℓ. The effect of the phase shift (which is an advance of phase) is to make the thorium atom appear to be closer to the X-ray source and detector than it really is. The symmetry of the space group gives a cancellation of the effect on x and y coordinates, but there is a systematic

Table 3. Atomic coordinates and estimated standard deviations

All values have been multiplied by 10^4.

Atom	x	y	z
Th	0	0	0
O(1)	0	0	2277(17)
O(2)	-0042(11)	1041(4)	0656(11)
O(3)	4543(11)	-0892(5)	-1066(12)
N(1)	2651(10)	0046(6)	0508(12)
O(11)	2094(9)	-0381(4)	0025(15)
O(12)	1970(10)	0453(5)	0915(13)
O(13)	3733(8)	0093(5)	0538(13)
N(2)	0471(12)	0772(5)	-2259(17)
O(21)	1318(9)	0551(5)	-1619(12)
O(22)	0579(9)	-0631(4)	-1924(12)
O(23)	0677(12)	1066(6)	-3213(12)

Table 4. Anisotropic thermal parameters

T.F. = $\exp(-\beta_{11}h^2 - 2\beta_{12}hk - \ldots)$; $4\beta_{12} = B_{12}a^*b^*$, etc. Standard deviations estimated by least squares are less than 0.05 for Th and from 0.3 to 0.8 for the other atoms.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Th	1.2	1.4	2.1	0.0	---	---
O(1)	4.5	2.0	3.7	0.9	---	---
O(2)	2.1	2.0	4.3	-0.3	0.0	-0.5
O(3)	2.4	2.6	3.3	0.1	-0.6	-0.2
N(1)	1.5	2.0	2.9	0.5	-0.5	-0.5
O(11)	2.2	1.4	3.8	0.8	-0.6	-0.7
O(12)	2.3	2.5	3.7	0.3	-0.2	-0.5
O(13)	1.0	2.8	5.2	-0.1	-0.5	0.0
N(2)	2.1	2.0	4.4	-0.9	0.3	0.2
O(21)	1.3	2.9	3.9	0.2	-0.3	0.9
O(22)	1.7	1.7	3.8	-0.2	0.4	-0.1
O(23)	3.5	3.6	3.0	-0.2	1.1	1.5

biasing of the z components of interatomic vectors between thorium and the rest of the structure.

This kind of shift will be a general feature of polar structures which are refined with such incomplete data, unless one of several obvious steps is taken to prevent it.

The two structures of opposite polarity are not different in the sense of right and left handedness, but only with respect to their orientation in a specimen. We have not made a correlation of the polarity with respect to morphology or other physical property.

Comparison with neutron diffraction results

The neutron diffraction study by Taylor, Mueller & Hitterman (196x) gives us a chance to check the accuracy of the X-ray method in a case where the heavy atom dominates the data. The agreement of the coordinates is excellent, and it confirms that the estimated standard deviations are of the correct magnitude. Of 31 independent coordinates, 17 are within one standard deviation and none is as much as three standard deviations from the corresponding neutron result. The atomic positions in the two structures differ by 0.026 Å on the average and by 0.045 Å in the most extreme case.

The structure obtained before correction for the thorium phase shift is in significantly poorer agreement with the neutron results; the average distance between atomic locations is 0.065 Å.

The neutron results show that each hydrogen location (Table 1) is in the correct neighborhood, but indicate errors of 0.2 to 0.5 Å from the correct position.

Discussion of the structure

Some interatomic distances are listed in Table 5. The thorium atom has its 11 oxygen neighbors arranged in a highly unsymmetrical way with respect to the polar direction (Fig. 1). These oxygen atoms are two each from four nitrate groups and three from water molecules, with all the water on one side. This polar arrangement is probably related to the large pyroelectric effect which is observed when the crystals are dipped in liquid nitrogen. One expects about 8 oxygen neighbors for thorium if the oxygen atoms are not bonded to each other. Two oxygen atoms in nitrate are closer than normal for atoms from separate molecules, and thus the coordination can be as high as 12 if the atoms are from six nitrate groups as in $MgTh(NO_3)_6 \cdot 8H_2O$ (Ščavničar & Prodić, 1965). Thus to have 11 neighbors is reasonable if 8 of them are from nitrate ions.

In each nitrate ion the non-coordinated oxygen atom is significantly closer to nitrogen than are the other two. A similar effect is observed in several other nitrate crystals as listed by Taylor, Mueller & Hitterman (196x), as well as in $Ce(NO_3)_3 \cdot 6H_2O$ and $Ce(NH_4)_2(NO_3)_6$ (Ueki, Zalkin & Templeton, unpublished). The terminal oxygen atom, in each case which we have studied, has higher thermal parameters than the other two. Thus a correction of bond distance for thermal motion removes some of the difference, but this correction seems to be inadequate to explain as much as half of the effect. In the present case, the thermal effect is estimated to account for about 0.01 Å of the difference.

We recognize five hydrogen bonds (Table 5) which are completely confirmed by the neutron diffraction results. Their distances and angles

Table 5. Bond lengths in Å, uncorrected for thermal motion

Values found by Taylor, Mueller & Hitterman are given in parentheses.

	Th-O (nitrate)	
Th-O(11)	2.50 ± 0.01	(2.528)
Th-O(12)	2.62 ± 0.01	(2.618)
Th-O(21)	2.59 ± 0.01	(2.573)
Th-O(22)	2.58 ± 0.01	(2.554)
	Th-O (water)	
Th-O(1)	2.41 ± 0.02	(2.438)
Th-O(2)	2.48 ± 0.01	(2.473)
	Nitrate groups	
N(1)-O(11)	1.27 ± 0.02	(1.270)
N(1)-O(12)	1.28 ± 0.02	(1.250)
N(1)-O(13)	1.21 ± 0.01	(1.202)
N(2)-O(21)	1.27 ± 0.02	(1.264)
N(2)-O(22)	1.27 ± 0.02	(1.275)
N(2)-O(23)	1.24 ± 0.02	(1.206)
	Hydrogen bonds	
O(1)-O(3)	2.74 ± 0.02	(2.698)
O(2)-O(3)	2.71 ± 0.02	(2.697)
O(2)-O(22)	2.90 ± 0.02	(2.953)
O(3)-O(23)	2.86 ± 0.02	(2.901)
O(3)-O(13)	2.96 ± 0.02	(2.946)

(Table 6) are normal. The hydrogen bonds to O(1), because of the two-fold axis, are exactly coplanar with the Th-O(1) bond and at equal angles to it. The hydrogen bonds to O(2) are very nearly coplanar with the Th-O(2) bond. This arrangement, with the water dipoles pointed almost directly away from the cation, is not surprising for such a highly charged ion. The water molecules in $Zr(SO_4)_2 \cdot 4H_2O$ are similarly oriented (Templeton, 1960). The water molecules designated as O(3) are bonded to the rest of the structure by four hydrogen bonds in directions corresponding to a rather distorted tetrahedron.

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Table 6. Bond angles

Atoms	Angle
Th-O(1)-O(3)	129.8 ± 0.4°
O(3)-O(1)-O(3)	100.4 ± 0.8°[a]
Th-O(2)-O(3)	124.0 ± 0.5°
Th-O(2)-O(22)	127.2 ± 0.5°
O(3)-O(2)-O(22)	108.7 ± 0.5°[a]
O(1)-O(3)-O(2)	108.4 ± 0.5°
O(1)-O(3)-O(13)	81.7 ± 0.5°
O(1)-O(3)-O(23)	103.9 ± 0.5°
O(2)-O(3)-O(13)	106.5 ± 0.5°
O(2)-O(3)-O(23)	124.6 ± 0.6°
O(13)-O(3)-O(23)	121.9 ± 0.5°[a]

[a] O...H-O-H...O angles.

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Figure caption

Fig. 1. Neighbors of the thorium atom in $Th(NO_3)_4 \cdot 5H_2O$.
W1 and W2 indicate water molecules called O(1) and O(2) in the text.