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Redetermination of the crystal structure of ThI_4

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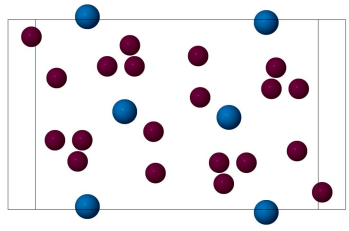
Single crystals of ThI_4, thorium(IV) tetraiodide, were grown from thorium dioxide and aluminium triiodide. In comparison with the structure model reported previously for this compound [Zalkin *et al.* (1964). *Inorg. Chem.* **3**, 639–644], we have determined the lattice parameters and fractional coordinates to a much higher precision, also leading to a better reliability factor ($R = 0.029$ *versus* 0.09). The coordination number of the Th^{IV} atom is eight. Its coordination polyhedron has the shape of an irregular square antiprism. The I atoms each bridge two Th^{IV} atoms, resulting in the formation of infinite layers parallel to $(\bar{1}01)$ that can be described with the Niggli formula $^{2}_{\infty}[ThI_{6/2}I_{2/2}]$.

3D view



Structure description

ThI_4 was first synthesized in 1882 (Nilson, 1882) by heating thorium metal in I_2 vapour. Its crystal structure has been known since 1964 (Zalkin *et al.*, 1964) and IR and Raman spectra were measured in 1976 (Brown *et al.*, 1976). The other tetrahalides of thorium, *viz*. ThF_4 (von Wartenberg *et al.*, 1923), $ThCl_4$ (Matignon & Delepine, 1907), $ThBr_4$ (Nilson, 1882), and the bi- and trivalent compounds ThI_2 (Anderson & D'Eye, 1949) and ThI_3 (Hayek & Rehner, 1949) are also known. In our efforts to synthesize pure actinide halides, we have developed a chemical vapour-transport method (Deubner *et al.*, 2017), which allowed us to obtain single crystals suitable for X-ray diffraction experiments.

The lattice parameters obtained by our single-crystal structure determination (Table 1) agree with those obtained previously ($a = 13.22$, $b = 8.07$, $c = 7.77$ Å, $\beta = 98.68°$, $Z = 4$, $T =$ n.a.; Zalkin *et al.*, 1964). The Th^{IV} atom is located on a general position and has eight iodine atoms in its irregular square-antiprismatic coordination sphere (Fig. 1). The Th—I distances range between 3.1324 (7) and 3.2896 (7) Å and are in good agreement with the previously reported data (3.128–3.291 Å; Zalkin *et al.*, 1964). As might be expected, the Th—I distances are comparable with those reported for the crystal structure of $ThTe_2I_2$

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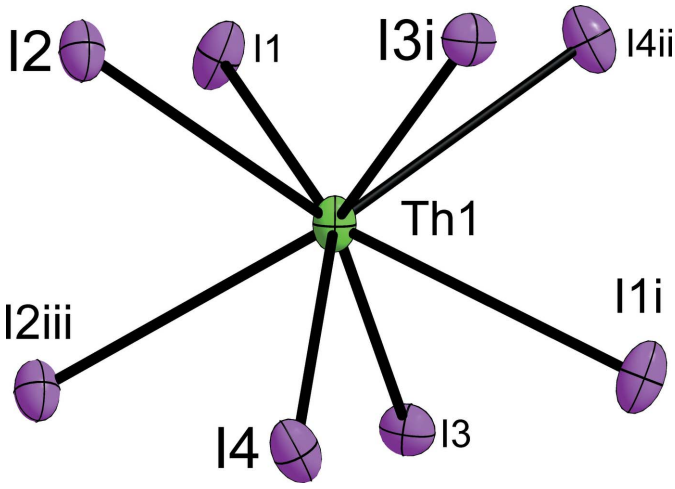

Figure 1
The irregular square-antiprismatic coordination sphere of the Th^{IV} atom in the crystal structure of ThI_4. Displacement ellipsoids are shown at the 95% probability level. [Symmetry codes: (i) $x, y-1, z$; (ii) $x, y-1, z-1$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $-x, -y+1, -z+1$.]

which features a similar anti-prismatic coordination sphere for the Th^{IV} atom [3.1445 (9)–3.2157 (7) Å; Rocker & Tremel, 2001]. The same applies for the Th···Th distances [4.4770 (6) Å] and the shortest I···I distances between the layers ranging from 4.1526 (8) to 4.2423 (8) Å [Th···Th distance: 4.478 (5), I···I distances: 4.079–4.252 (6) Å; Zalkin *et al.*, 1964). The I—I—I angles (Table 1) of the irregular polyhedron faces are also in good agreement with the previous structure determination (Zalkin *et al.*, 1964).

With respect to the shortest Th···Th distance of 4.4770 (6) Å, the Th^{IV} atoms are bridged by three iodide atoms (a triangular face of the square antiprism formed by the I2, I3 and I4 atoms), formally leading to the formation of one-dimensional infinite chains. These chains are in turn interconnected by shared edges of the antiprism (the I1 atoms), which corresponds to a Th···Th distance of 5.1998 (8) Å. This connection leads to infinite layers of $^{2}_{\infty}[ThI_{6/2}I_{2/2}]$, running parallel to $(\bar{1}01)$ (Fig. 2). The arrangement of the Th^{IV} atoms within a layer corresponds to a 6^3 network. Fig. 3 shows the crystal structure of the compound.

Table 1
The I—I—I angles (°) within the irregular ThI_8 coordination polyhedron.

Face	Present refinement	Previous refinement (Zalkin *et al.*, 1964)
$I2—I1^{iv}—I3^{i}$	76.510 (15)	76.5
$I1^{iv}—I3^{i}—I4^{iii}$	101.411 (17)	101.5
$I3^{i}—I4^{iii}—I2$	79.585 (15)	79.5
$I4^{iii}—I2—I1^{iv}$	97.949 (16)	98.0
$I4—I1^{ii}—I2^{iii}$	87.142 (16)	87.0
$I2^{iii}—I3^{iii}—I4$	91.545 (16)	91.5
$I1^{ii}—I2^{iii}—I3^{iii}$	91.485 (16)	91.4
$I1^{ii}—I4—I3^{iii}$	89.821 (15)	90.0

Symmetry codes: (i) $x, y-1, z$; (ii) $x, y-1, z-1$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x, -y+1, -z+1$.

Synthesis and crystallization

Thorium(IV) tetraiodide was synthesized from dry thorium dioxide (3.00 g, 11.36 mmol, Merck) and sublimed aluminium iodide (9.28 g, 22.76 mmol) in an evacuated and flame-sealed borosilicate tube at 623 K with an additional *in situ* chemical vapour transport (Deubner *et al.*, 2017). The temperature at the source region was 723 K and at the sink region 623 K; the length of the tube was 13 cm. Canary yellow crystals could be obtained by an additional vacuum sublimation at 723 K in an evacuated, flame-sealed borosilicate tube.

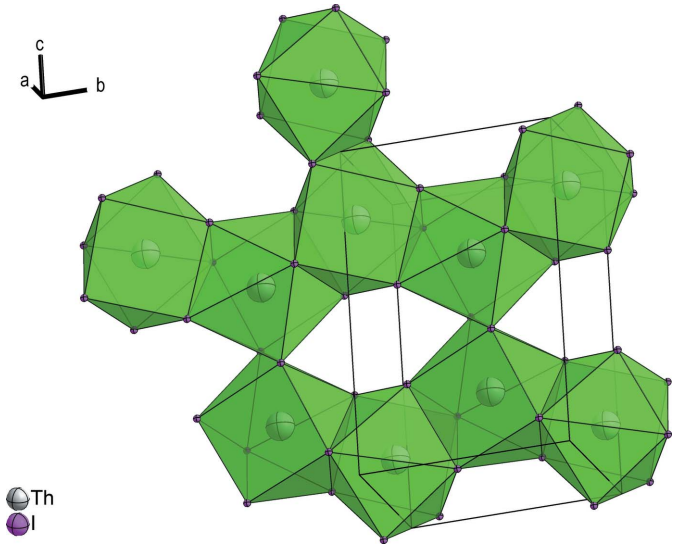

Figure 2
A section of the $^{2}_{\infty}[ThI_{6/2}I_{2/2}]$ layer within the crystal structure of ThI_4, showing the connection of the coordination polyhedra *via* faces and edges. Coordination polyhedra are shown transparent in green, atomic radii are arbitrary.

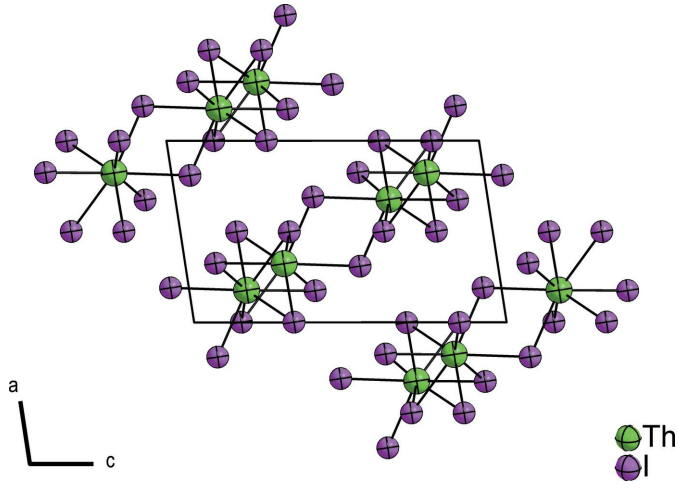

Figure 3
The crystal structure of ThI_4 in a projection along [010]. Displacement ellipsoids are shown at the 95% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	ThI_4
M_r	739.64
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	243
a, b, c (Å)	13.1903 (16), 8.0686 (12), 7.755 (1)
β (°)	98.619 (10)
V (Å^3)	816.02 (19)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	33.29
Crystal size (mm)	0.39 × 0.26 × 0.14
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Numerical (*X-RED* and *X-SHAPE*; Stoe & Cie, 2009)
T_{min}, T_{max}	0.240, 0.622
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5880, 2174, 1988
R_{int}	0.063
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.688
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.071, 1.18
No. of reflections	2174
No. of parameters	47
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.82, −2.06

Computer programs: *X-AREA* (Stoe & Cie, 2011) *X-RED* (Stoe & Cie, 2009), *SHELXL2018* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2015) and *publCIF* (Westrip, 2010). Coordinates taken from a previous model.

Refinement

As a starting model for the structure refinement, the atomic coordinates of the previously reported ThI_4 structure were used (Zalkin *et al.*, 1964). Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2018). **3**, x180201 [https://doi.org/10.1107/S2414314618002018]

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Thorium tetraiodide

Crystal data

ThI_4
M_r = 739.64
Monoclinic, $P2_1/n$
a = 13.1903 (16) Å
b = 8.0686 (12) Å
c = 7.755 (1) Å
β = 98.619 (10)°
V = 816.02 (19) Å^3
Z = 4
F(000) = 1208
cell choice according to the previous literature
D_x = 6.020 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6166 reflections
θ = 4.9–58.3°
μ = 33.29 mm^{-1}
T = 243 K
Hexagonal-block, canary yellow
0.39 × 0.26 × 0.14 mm

Data collection

Stoe IPDS 2T diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Graphite monochromator
rotation method scans
Absorption correction: numerical (*X-RED* and *X-SHAPE*; Stoe & Cie, 2009)
T_{min} = 0.240, T_{max} = 0.622
5880 measured reflections
2174 independent reflections
1988 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 29.3°, θ_{min} = 2.9°
h = −18→18
k = −11→9
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.071
S = 1.18
2174 reflections
47 parameters
0 restraints
0 constraints
Primary atom site location: isomorphous structure methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.82 e Å^{-3}
$\Delta\rho_{min}$ = −2.06 e Å^{-3}
Extinction correction: SHELXL2018 (Sheldrick, 2015), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00252 (18)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Th1	0.18352 (2)	0.01507 (3)	0.17681 (3)	0.01185 (10)
I1	0.05855 (4)	0.90966 (7)	0.80945 (6)	0.01692 (12)
I2	0.18029 (4)	0.25357 (6)	0.49875 (6)	0.01548 (12)
I3	0.09726 (4)	0.69187 (6)	0.32569 (6)	0.01769 (13)
I4	0.15132 (4)	0.36459 (6)	0.00132 (6)	0.01833 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Th1	0.01200 (14)	0.00591 (15)	0.01672 (14)	−0.00018 (8)	−0.00090 (8)	−0.00035 (8)
I1	0.0137 (2)	0.0170 (3)	0.0190 (2)	0.00123 (17)	−0.00083 (15)	−0.00413 (17)
I2	0.0177 (2)	0.0117 (2)	0.0173 (2)	−0.00222 (16)	0.00343 (15)	−0.00095 (16)
I3	0.0134 (2)	0.0108 (3)	0.0290 (3)	0.00061 (16)	0.00340 (17)	0.00347 (18)
I4	0.0218 (2)	0.0100 (2)	0.0202 (2)	−0.00236 (17)	−0.00671 (17)	0.00211 (16)

Geometric parameters (Å, º)

Th1—I4	3.1324 (7)	Th1—I3^{iii}	3.2269 (6)
Th1—I3^{i}	3.1340 (6)	Th1—I1^{iv}	3.2675 (6)
Th1—I2	3.1576 (6)	Th1—I4^{iii}	3.2896 (7)
Th1—I1^{ii}	3.1857 (7)	Th1—Th1^{v}	4.4770 (6)
Th1—I2^{iii}	3.2041 (6)	Th1—Th1^{vi}	5.1998 (8)
I4—Th1—I3^{i}	151.181 (15)	I3^{iii}—Th1—I4^{iii}	71.069 (16)
I4—Th1—I2	77.164 (17)	I1^{iv}—Th1—I4^{iii}	125.668 (16)
I3^{i}—Th1—I2	99.624 (17)	I4—Th1—Th1^{v}	47.262 (12)
I4—Th1—I1^{ii}	80.418 (16)	I3^{i}—Th1—Th1^{v}	143.752 (15)
I3^{i}—Th1—I1^{ii}	86.534 (16)	I2—Th1—Th1^{v}	45.695 (11)
I2—Th1—I1^{ii}	143.446 (15)	I1^{ii}—Th1—Th1^{v}	126.717 (13)
I4—Th1—I2^{iii}	117.155 (16)	I2^{iii}—Th1—Th1^{v}	118.545 (15)
I3^{i}—Th1—I2^{iii}	82.309 (17)	I3^{iii}—Th1—Th1^{v}	44.426 (10)
I2—Th1—I2^{iii}	144.308 (10)	I1^{iv}—Th1—Th1^{v}	99.896 (13)
I1^{ii}—Th1—I2^{iii}	72.070 (15)	I4^{iii}—Th1—Th1^{v}	87.161 (14)
I4—Th1—I3^{iii}	70.287 (15)	I4—Th1—Th1^{vi}	76.002 (12)
I3^{i}—Th1—I3^{iii}	138.169 (14)	I3^{i}—Th1—Th1^{vi}	78.151 (12)
I2—Th1—I3^{iii}	81.582 (15)	I2—Th1—Th1^{vi}	108.886 (14)
I1^{ii}—Th1—I3^{iii}	117.173 (16)	I1^{ii}—Th1—Th1^{vi}	36.853 (10)
I2^{iii}—Th1—I3^{iii}	74.250 (16)	I2^{iii}—Th1—Th1^{vi}	106.387 (14)
I4—Th1—I1^{iv}	77.136 (15)	I3^{iii}—Th1—Th1^{vi}	141.428 (14)
I3^{i}—Th1—I1^{iv}	74.466 (15)	I1^{iv}—Th1—Th1^{vi}	35.786 (10)
I2—Th1—I1^{iv}	74.449 (15)	I4^{iii}—Th1—Th1^{vi}	147.277 (14)
I1^{ii}—Th1—I1^{iv}	72.639 (17)	Th1^{v}—Th1—Th1^{vi}	118.313 (9)
I2^{iii}—Th1—I1^{iv}	138.513 (15)	Th1^{vii}—I1—Th1^{iv}	107.361 (17)
I3^{iii}—Th1—I1^{iv}	143.026 (16)	Th1—I2—Th1^{v}	89.455 (15)
I4—Th1—I4^{iii}	133.886 (15)	Th1^{viii}—I3—Th1^{v}	89.458 (15)

I3^{i}—Th1—I4^{iii}	69.451 (15)	Th1—I4—Th1^{v}	88.361 (15)
I2—Th1—I4^{iii}	73.192 (16)	Th1—I4—I1^{ix}	161.270 (12)
I1^{ii}—Th1—I4^{iii}	140.814 (17)	Th1^{v}—I4—I1^{ix}	76.457 (11)
I2^{iii}—Th1—I4^{iii}	74.312 (15)		

Symmetry codes: (i) x, $y-1$, z; (ii) x, $y-1$, $z-1$; (iii) $-x+1/2$, $y-1/2$, $-z+1/2$; (iv) $-x$, $-y+1$, $-z+1$; (v) $-x+1/2$, $y+1/2$, $-z+1/2$; (vi) $-x$, $-y$, $-z$; (vii) x, $y+1$, $z+1$; (viii) x, $y+1$, z; (ix) x, $y+1$, $z-1$.