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Rerefinement of the crystal structure of α-$ThBr_4$

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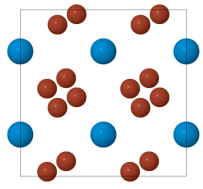
Single crystals of α-$ThBr_4$, thorium(IV) tetrabromide, were obtained as a side product from the reaction of CuBr with β-$ThBr_4$ at 753 K. In the crystal structure, the Th atom (site symmetry $\bar{4}$..) is surrounded by eight Br atoms in the form of a tetragonal-disphenoidal coordination polyhedron. The connectivity of these polyhedra is $^3_\infty[ThBr_{4/2}Br_{4/2}]$. In comparison with the previous crystal structure refinement [Mason *et al.* (1974). *J. Less-Common Met.* **35**, 331–338], the current rerefinement resulted in much higher preciscion of the lattice parameters and the atomic coordinates.

3D view



Structure description

A crystal of $ThBr_4$ in its α-modification was isolated as a side product from the reaction of β-$ThBr_4$ with CuBr at 753 K.

The crystal structure of α-$ThBr_4$ has been described only once, from a single-crystal X-ray diffraction study at room temperature (Mason *et al.*, 1974), where the authors refer to this modification also as the low-temperature polymorph. They reported the transition temperature at 699 ± 5 K and the crystal structure of α-$ThBr_4$ was assigned to the α-$ThCl_4$ structure type in the space group $I4_1/a$ (No. 88, $tI20$). A comparison of the structural parameters of the original crystal structure refinement and of the current rerefinement is given in Table 1.

Fig. 1 shows the crystal structure based on the current X-ray diffraction data. There is one Th atom (multiplicity 4, Wyckoff letter *a*, site symmetry $\bar{4}$..) and one Br atom (16*f*, site symmetry 1) in the asymmetric unit. The Th atom is surrounded by eight Br atoms to form a tetragonal-disphenoidal coordination polyhedron. The Th—Br bond lengths of 4×2.9100 (4) Å and 4×3.0107 (4) Å are in good agreement with previously reported values of 2.909 and 3.020 Å (no s.u. values or temperature given; Mason *et al.*, 1974), but different compared to those in β-$ThBr_4$ (space group $I4_1/amd$), with values of 2.85 and 3.12 Å (no s.u. values or temperature given; Brown *et al.*, 1973). Each Br atom bridges two Th atoms, which results in edge-sharing polyhedra to form the crystal structure. The connection motif of α-$ThBr_4$ is similar to that in β-$ThBr_4$. Although the two polymorphs

Table 1
Comparison of structural parameters of α-$ThBr_4$ resulting from the current and previous crystal structure refinements.

	This work	Mason *et al.* (1974)
a (Å)	6.7068 (2)	6.737 (1)
c (Å)	13.5792 (6)	13.601 (3)
x, y, z Th	0, 1/4, 1/8	0, 1/4, 1/8
x, y, z Br	0.33880 (6), 0.47423 (6), 0.20021 (3)	0.3378 (6), 0.4727 (7), 0.1998 (3)

differ considerably with respect to the two pairs of Th—Br distances, the connectivities in both structures can be described with the Niggli formula $^3_\infty[ThBr_{4/2}Br_{4/2}]$. The closest Th···Th distance of 4.77179 (12) Å in α-$ThBr_4$ is shorter compared to β-$ThBr_4$, with a value of 4.8774 Å (Brown *et al.*, 1973). In the crystal structure of α-$ThBr_4$, each Th atom is surrounded by eight other Th atoms in the shape of an irregular polyhedron, with Th···Th distances of 4 × 4.77179 (12) Å and 4 × 6.70680 (19) Å.

Synthesis and crystallization

All work was carried under an argon atmosphere (5.0, Praxair) using a fine-vacuum line and a glove-box (MBraun). Silica ampoules were flame-dried under dynamic fine vacuum (10^{-3} mbar; 1 bar = 10^5 Pa) at least three times before use. Aluminium bromide (Alfa Aesar, 98%) was sublimed *in vacuo* before use; β-$ThBr_4$ was prepared according to a literature protocol (Deubner *et al.*, 2017).

A silica glass ampoule was loaded with β-$ThBr_4$ (149 mg, 0.27 mmol) and CuBr (78 mg, 54 mmol, 2.01 equiv.), and sealed under vacuum. The ampoule was heated in a furnace to 753 K at a rate of 1 K min^{-1} and kept at this temperature for 480 h for the reaction to take place. Afterwards, it was cooled to 330 K at a rate of 50 K d^{-1}. Several colourless crystals of α-$ThBr_4$ were obtained.

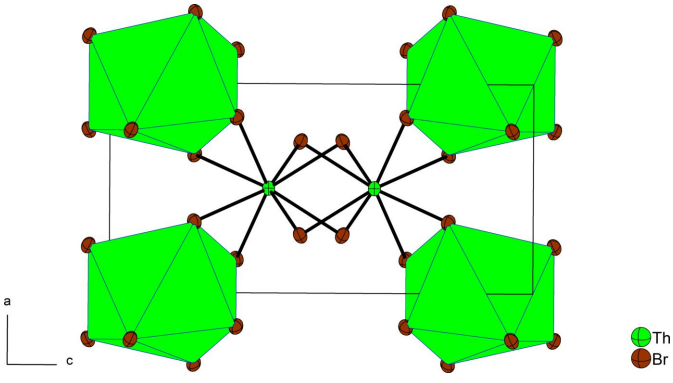


Figure 1
Crystal structure of α-$ThBr_4$ in a projection along [010]. Displacement ellipsoids are drawn at the 90% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$ThBr_4$
M_r	551.68
Crystal system, space group	Tetragonal, $I4_1/a$
Temperature (K)	100
a, c (Å)	6.7068 (2), 13.5792 (6)
V (Å^3)	610.81 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	50.43
Crystal size (mm)	0.15 × 0.15 × 0.14
Data collection	
Diffractometer	Bruker D8 QUEST
Absorption correction	Numerical (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.016, 0.078
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9305, 463, 463
R_{int}	0.049
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.053, 1.37
No. of reflections	463
No. of parameters	13
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.16, −1.72

Computer programs: *APEX3* and *SAINT* (Bruker, 2019), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2022) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

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alpha-Thorium(IV) tetrabromide

Crystal data

$ThBr_4$
M_r = 551.68
Tetragonal, $I4_1/a$
a = 6.7068 (2) Å
c = 13.5792 (6) Å
V = 610.81 (5) Å^3
Z = 4
$F(000)$ = 920
D_x = 5.999 Mg m^{-3}
Melting point: 200 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9713 reflections
θ = 3.0–30.6°
μ = 50.43 mm^{-1}
T = 100 K
Block, colorless
0.15 × 0.14 × 0.14 mm

Data collection

Bruker D8 QUEST diffractometer
Radiation source: Incoatec Microfocus
Multi layered optics monochromator
Detector resolution: 10.42 pixels mm^{-1}
φ and ω scans
Absorption correction: numerical (SADABS; Krause *et al.*, 2015)
T_{min} = 0.016, T_{max} = 0.078
9305 measured reflections
463 independent reflections
463 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 30.5°, θ_{min} = 5.2°
h = −9→9
k = −9→9
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.053
S = 1.37
463 reflections
13 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0219P)^2 + 6.5321P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.16 e Å^{-3}
$\Delta\rho_{min}$ = −1.72 e Å^{-3}
Extinction correction: SHELXL (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0052 (4)

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	0.000000	0.250000	0.125000	0.00764 (15)
Br1	0.33880 (6)	0.47423 (6)	0.20021 (3)	0.00953 (16)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Th1	0.00844 (17)	0.00844 (17)	0.00604 (19)	0.000	0.000	0.000
Br1	0.0101 (2)	0.0104 (2)	0.0080 (2)	−0.00131 (13)	−0.00114 (13)	0.00179 (13)

Geometric parameters (Å, º)

Th1—Br1	2.9100 (4)	Th1—Br1^{iv}	3.0107 (4)
Th1—Br1^{i}	2.9100 (4)	Th1—Br1^{v}	3.0107 (4)
Th1—Br1^{ii}	2.9100 (4)	Th1—Br1^{vi}	3.0107 (4)
Th1—Br1^{iii}	2.9100 (4)	Th1—Br1^{vii}	3.0107 (4)
Br1—Th1—Br1^{i}	138.907 (16)	Br1—Th1—Br1^{vi}	72.606 (12)
Br1—Th1—Br1^{ii}	97.075 (5)	Br1^{i}—Th1—Br1^{vi}	75.260 (8)
Br1^{i}—Th1—Br1^{ii}	97.075 (5)	Br1^{ii}—Th1—Br1^{vi}	72.605 (8)
Br1—Th1—Br1^{iii}	97.076 (5)	Br1^{iii}—Th1—Br1^{vi}	148.466 (14)
Br1^{i}—Th1—Br1^{iii}	97.075 (5)	Br1^{iv}—Th1—Br1^{vi}	128.427 (10)
Br1^{ii}—Th1—Br1^{iii}	138.907 (16)	Br1^{v}—Th1—Br1^{vi}	75.934 (16)
Br1—Th1—Br1^{iv}	148.466 (14)	Br1—Th1—Br1^{vii}	72.605 (8)
Br1^{i}—Th1—Br1^{iv}	72.605 (8)	Br1^{i}—Th1—Br1^{vii}	148.466 (14)
Br1^{ii}—Th1—Br1^{iv}	72.606 (12)	Br1^{ii}—Th1—Br1^{vii}	75.260 (8)
Br1^{iii}—Th1—Br1^{iv}	75.260 (8)	Br1^{iii}—Th1—Br1^{vii}	72.606 (12)
Br1—Th1—Br1^{v}	75.260 (8)	Br1^{iv}—Th1—Br1^{vii}	75.934 (16)
Br1^{i}—Th1—Br1^{v}	72.606 (12)	Br1^{v}—Th1—Br1^{vii}	128.427 (10)
Br1^{ii}—Th1—Br1^{v}	148.466 (14)	Br1^{vi}—Th1—Br1^{vii}	128.427 (10)
Br1^{iii}—Th1—Br1^{v}	72.605 (8)	Th1—Br1—Th1^{vi}	107.394 (12)
Br1^{iv}—Th1—Br1^{v}	128.427 (10)		

Symmetry codes: (i) −*x*, −*y*+1/2, *z*; (ii) *y*−1/4, −*x*+1/4, −*z*+1/4; (iii) −*y*+1/4, *x*+1/4, −*z*+1/4; (iv) −*y*+1/4, *x*−1/4, *z*−1/4; (v) *x*−1/2, *y*, −*z*+1/2; (vi) −*x*+1/2, −*y*+1/2, −*z*+1/2; (vii) *y*−1/4, −*x*+3/4, *z*−1/4.