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Crystal structure of $\text{Cs}_2[\text{Th}(\text{NO}_3)_6]$

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Dicaesium hexanitratothorate(IV), $\text{Cs}_2[\text{Th}(\text{NO}_3)_6]$, was synthesized in the form of colourless crystals by reaction of thorium nitrate and caesium nitrate in aqueous solution. The Th atom is located on an inversion centre and is coordinated by six chelating nitrate anions. The resulting ThO_{12} coordination polyhedron is best described as a slightly distorted icosahedron. The Cs atom also has a coordination number of 12, but its coordination polyhedron is considerably more distorted. The crystal packing can be derived from an hexagonal dense packing (hcp) of idealized spherical CsO_{12} and ThO_{12} units. The CsO_{12} units form a distorted hcp arrangement and half of the octahedral sites are occupied by the ThO_{12} units.

1. Chemical context

Nitrato complexes of the actinoids (Ryan, 1961; Strnad & Kohler, 1989) play an important role in the production of nuclear fuel as well as in its reprocessing. Moreover, multinary thorium nitrate compounds are of potential interest as anhydrous starting materials for further chemical conversion.

2. Structural commentary

The thorium atom, Th1, occupies Wyckoff position $2c$ and has site symmetry $\bar{1}$. It is coordinated by six chelating nitrate anions in general positions. The resulting ThO_{12} polyhedron can be best described as a slightly distorted icosahedron. The $[\text{Th}(\text{NO}_3)_6]^{2-}$ -anion is shown in Fig. 1. Its Th—O distances are in a rather narrow range from 2.541 (2) to 2.581 (2) Å and

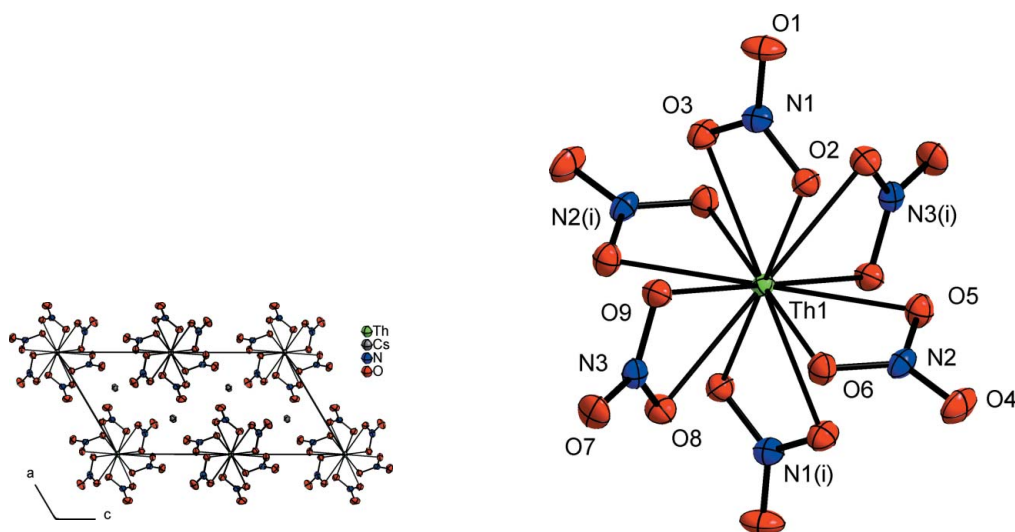


Figure 1
The $[\text{Th}(\text{NO}_3)_6]^{2-}$ -anion of the title compound. Displacement ellipsoids are drawn at the 70% probability level. Labelling for symmetry-equivalent oxygen atoms is omitted for clarity. [Symmetry code: (i) $-x, -y + 1, -z$.]

compare quite well with Th—O distances of other reported thorium nitrate structures. In $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_4$, they range from 2.54 (1) to 2.61 (1) Å (Charpin *et al.*, 1987), in $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_5$ from 2.50 (1) to 2.62 (1) Å (Ueki *et al.*, 1966; Taylor *et al.*, 1966), and in the cubic structure of $\text{K}_2[\text{Th}(\text{NO}_3)_6]$ Th—O distances ranging from 2.535 (2) to 2.581 (2) Å were reported (Sigmon & Burns, 2010).

In the nitrate ligands, the N—O distances of the metal-coordinating oxygen atoms are, as expected, elongated [1.270 (3) to 1.287 (3) Å] compared to the N—O distances of the terminal oxygen atoms [1.210 (3) to 1.212 (3) Å]. Similar N—O distances were reported for the nitrate anions in $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_4$ (Charpin *et al.*, 1987), $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_5$ (Ueki *et al.*, 1966; Taylor *et al.*, 1966) and $\text{K}_2[\text{Th}(\text{NO}_3)_6]$ (Sigmon & Burns, 2010).

The An —O ($An = \text{Th}$) and N—O distances in the title compound are also comparable to the respective distances reported for the uranyl nitrate $\text{Rb}(\text{UO}_2)(\text{NO}_3)_3$ (Zalkin *et al.*, 1989), with 2.474 (3) Å for An —O ($An = \text{U}$), 1.205 (6) Å for terminal N—O, and 1.268 (4) Å for the metal-coordinating oxygen atoms. The crystal chemistry of $M[\text{UO}_2(\text{NO}_3)_3]$ ($M = \text{K}, \text{Rb}$, and Cs) compounds, with $M = \text{K}$ (Jouffret *et al.*, 2011; Krivovichev & Burns, 2004), Rb (Barclay *et al.*, 1965; Zalkin *et al.*, 1989) and Cs (Malcic & Ljubica, 1961), was discussed comparatively by Krivovichev & Burns (2004).

The caesium cation is surrounded by eleven NO_3^- -anions, one of which is chelating, leading to an overall coordination number of 12. The Cs—O distances of the chelating O-atoms range from 3.150 (2) to 3.436 (3) Å, whereas the other ten Cs—O distances are between 3.090 (2) and 3.552 (2) Å.

The crystal structure of $\text{Cs}_2[\text{Th}(\text{NO}_3)_6]$ can be derived from a dense packing if the CsO_{12} and ThO_{12} units are idealized as spheres. The CsO_{12} units form a distorted hexagonal close-packed arrangement with the ThO_{12} units situated in half of the octahedral sites. The unit cell of $\text{Cs}_2[\text{Th}(\text{NO}_3)_6]$ is shown in Fig. 2, pointing out the pseudo-hexagonal arrangement.

The structure of the title compound is assumed to be isotypic with that of $\text{Rb}_2[\text{Th}(\text{NO}_3)_6]$ (Walker *et al.*, 1956), although atom positions have not been reported for the Rb

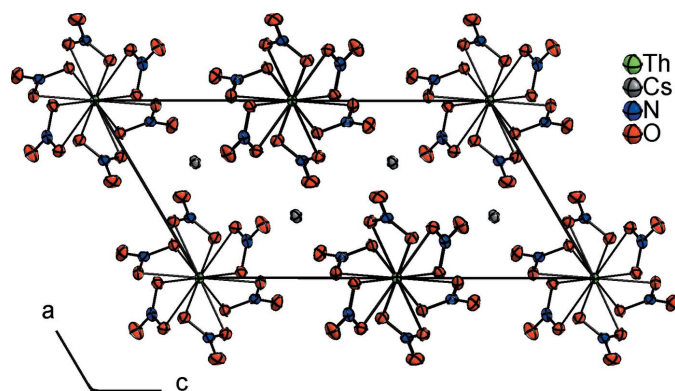


Figure 2
Unit cell of $\text{Cs}_2[\text{Th}(\text{NO}_3)_6]$ viewed along [010]. Displacement ellipsoids are shown at the 70% probability level.

Table 1
Experimental details.

Crystal data	
Chemical formula	$\text{Cs}_2[\text{Th}(\text{NO}_3)_6]$
M_r	869.92
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	123
a, b, c (Å)	8.1259 (14), 7.1873 (12), 15.583 (3)
β (°)	120.631 (10)
V (Å ³)	783.1 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	14.22
Crystal size (mm)	0.09 × 0.07 × 0.06
Data collection	
Diffractometer	Bruker Kappa APEXII
Absorption correction	Multi-scan (SADABS; Bruker, 2008)
T_{\min}, T_{\max}	0.374, 0.498
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31379, 3684, 2913
R_{int}	0.043
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.831
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.023, 0.047, 1.04
No. of reflections	3684
No. of parameters	124
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	2.14, -1.35

Computer programs: APEX2 and SAINT (Bruker, 2008), SHELXS97 and SHELXL97 (Sheldrick, 2008), SHELXLE (Hübschle *et al.*, 2011), DIAMOND (Brandenburg, 2012) and publCIF (Westrip, 2010).

compound so far. However, the unit cells are similar and the space group types are identical.

3. Synthesis and crystallization

0.1 g (0.18 mmol, 1 eq) $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and 70 mg (0.36 mmol, 2 eq) CsNO_3 were placed in a reaction flask and 100 ml water were added. The turbid solution was stirred and 1 ml of HNO_3 conc. was additionally added, which led to a clear solution. The mixture was heated to 333 K and evaporated at 22 mbar in a rotary evaporator leading to a colourless powder. After dissolving the colourless solid in as little water as possible, the solution was allowed to evaporate at room temperature for one month. Single crystals of the title compound were obtained in an almost quantitative yield.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The highest remaining electron density was found in Wyckoff position $2a$. Inclusion of this density in the refinement led to unreasonable models. In the final model, this density was therefore not further considered.

Acknowledgements

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References

- Barclay, G. A., Sabine, T. M. & Taylor, J. C. (1965). *Acta Cryst.* **19**, 205–209.
- Brandenburg, K. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2008). *APEX2*, *SAINTE* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Charpin, P., Chevrier, G., Lance, M., Nierlich, M., Vigner, D., Livet, J. & Musikas, C. (1987). *Acta Cryst.* **C43**, 1239–1241.
- Hübschle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). *J. Appl. Cryst.* **44**, 1281–1284.
- Jouffret, L. J., Krivovichev, S. V. & Burns, P. C. (2011). *Z. Anorg. Allg. Chem.* **637**, 1475–1480.
- Krivovichev, S. V. & Burns, P. C. (2004). *Radiochemistry*, **46**, 16–19.
- Malcic, S. S. & Ljubica, L. M. (1961). *Bull. B. Kidric. Inst. Nucl. Sci.* **11**, 135–139.
- Ryan, J. L. (1961). *J. Phys. Chem.* **65**, 1099–1107.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sigmon, G. E. & Burns, P. C. (2010). *J. Solid State Chem.* **183**, 1604–1608.
- Strnad, J. & Kohler, H.-H. (1989). *Ber. Bunsen. Phys. Chem.* **93**, 1429–1432.
- Taylor, J. C., Mueller, M. H. & Hitterman, R. L. (1966). *Acta Cryst.* **20**, 842–851.
- Ueki, T., Zalkin, A. & Templeton, D. H. (1966). *Acta Cryst.* **20**, 836–841.
- Walker, D. J., Cromer, D. T. & Staritzky, E. (1956). *Anal. Chem.* **28**, 1635–1636.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Zalkin, A., Templeton, L. K. & Templeton, D. H. (1989). *Acta Cryst.* **C45**, 810–811.

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Crystal structure of Cs₂[Th(NO₃)₆]

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Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *SHELXLE* (Hübschle *et al.*, 2011); molecular graphics: *DIAMOND* (Brandenburg, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Dicaesium hexanitratothorate(IV)

Crystal data

Cs₂[Th(NO₃)₆]

$M_r = 869.92$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.1259$ (14) Å

$b = 7.1873$ (12) Å

$c = 15.583$ (3) Å

$\beta = 120.631$ (10)°

$V = 783.1$ (2) Å³

$Z = 2$

$F(000) = 772$

$D_x = 3.689$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9806 reflections

$\theta = 2.9$ – 36.0 °

$\mu = 14.22$ mm⁻¹

$T = 123$ K

Block, colourless

$0.09 \times 0.07 \times 0.06$ mm

Data collection

Bruker Kappa APEXII
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 16 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)

$T_{\min} = 0.374$, $T_{\max} = 0.498$

31379 measured reflections

3684 independent reflections

2913 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$

$\theta_{\max} = 36.2$ °, $\theta_{\min} = 2.9$ °

$h = -13 \rightarrow 13$

$k = -10 \rightarrow 11$

$l = -25 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.047$

$S = 1.04$

3684 reflections

124 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

$w = 1/[\sigma^2(F_o^2) + (0.0213P)^2 + 0.6529P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 2.14$ e Å⁻³

$\Delta\rho_{\min} = -1.35$ e Å⁻³

Special details

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

Refinement. Refinement of F^2 against all reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on all data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Th1	0.0000	0.5000	0.0000	0.00841 (3)
Cs1	0.65173 (2)	0.75443 (3)	0.162303 (12)	0.01352 (4)
N1	0.2073 (4)	0.7544 (4)	0.17622 (17)	0.0131 (4)
O1	0.2995 (3)	0.8680 (4)	0.24064 (17)	0.0209 (5)
O2	0.2851 (3)	0.6068 (3)	0.16636 (15)	0.0138 (4)
O3	0.0296 (3)	0.7724 (3)	0.11416 (15)	0.0151 (4)
N2	0.3383 (3)	0.2500 (4)	0.06501 (18)	0.0132 (4)
O4	0.4570 (3)	0.1358 (4)	0.07556 (18)	0.0216 (5)
O5	0.3172 (3)	0.4028 (3)	0.01760 (16)	0.0152 (4)
O6	0.2249 (3)	0.2274 (3)	0.09779 (16)	0.0151 (4)
N3	-0.1193 (3)	0.2394 (4)	0.10851 (18)	0.0119 (4)
O7	-0.1394 (3)	0.1225 (3)	0.15830 (16)	0.0174 (4)
O8	-0.1830 (3)	0.2212 (3)	0.01536 (15)	0.0146 (4)
O9	-0.0265 (3)	0.3910 (3)	0.14759 (15)	0.0139 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Th1	0.00943 (5)	0.00874 (7)	0.00772 (5)	0.00017 (5)	0.00486 (4)	-0.00012 (5)
Cs1	0.01532 (8)	0.01297 (9)	0.01191 (7)	-0.00162 (6)	0.00667 (6)	0.00070 (6)
N1	0.0167 (10)	0.0129 (12)	0.0101 (9)	-0.0014 (9)	0.0071 (8)	-0.0003 (8)
O1	0.0273 (12)	0.0148 (12)	0.0158 (10)	-0.0061 (9)	0.0076 (9)	-0.0058 (8)
O2	0.0136 (9)	0.0135 (11)	0.0143 (9)	0.0002 (7)	0.0070 (8)	-0.0007 (7)
O3	0.0145 (9)	0.0172 (12)	0.0119 (9)	0.0006 (8)	0.0055 (7)	-0.0025 (8)
N2	0.0119 (10)	0.0151 (13)	0.0116 (9)	0.0032 (9)	0.0051 (8)	-0.0006 (9)
O4	0.0168 (10)	0.0203 (13)	0.0247 (11)	0.0088 (9)	0.0086 (9)	-0.0010 (9)
O5	0.0156 (9)	0.0164 (12)	0.0151 (9)	0.0021 (8)	0.0089 (8)	0.0023 (8)
O6	0.0157 (9)	0.0154 (12)	0.0165 (9)	0.0014 (7)	0.0098 (8)	0.0021 (8)
N3	0.0111 (9)	0.0123 (12)	0.0130 (10)	0.0023 (8)	0.0066 (8)	0.0032 (8)
O7	0.0226 (11)	0.0143 (12)	0.0200 (10)	0.0010 (8)	0.0142 (9)	0.0063 (8)
O8	0.0159 (9)	0.0177 (12)	0.0101 (8)	-0.0033 (8)	0.0065 (7)	-0.0021 (7)
O9	0.0177 (9)	0.0143 (11)	0.0116 (9)	-0.0028 (8)	0.0088 (8)	-0.0015 (7)

Geometric parameters (Å, °)

Th1—O9	2.541 (2)	N1—O1	1.212 (3)
Th1—O9 ⁱ	2.541 (2)	N1—O3	1.270 (3)
Th1—O5	2.547 (2)	N1—O2	1.283 (3)
Th1—O5 ⁱ	2.547 (2)	O1—Cs1 ^{iv}	3.090 (2)
Th1—O2	2.561 (2)	O2—Cs1 ⁱⁱ	3.523 (2)
Th1—O2 ⁱ	2.561 (2)	O3—Cs1 ^{viii}	3.515 (2)
Th1—O3	2.573 (2)	N2—O4	1.212 (3)
Th1—O3 ⁱ	2.573 (2)	N2—O6	1.271 (3)
Th1—O8 ⁱ	2.578 (2)	N2—O5	1.285 (3)
Th1—O8	2.578 (2)	N2—Cs1 ^v	3.584 (2)
Th1—O6 ⁱ	2.581 (2)	O4—Cs1 ^{ix}	3.109 (3)
Th1—O6	2.581 (2)	O4—Cs1 ^v	3.436 (3)
Cs1—O1 ⁱⁱ	3.090 (2)	O5—Cs1 ^v	3.150 (2)
Cs1—O4 ⁱⁱⁱ	3.109 (3)	O6—Cs1 ⁱⁱ	3.347 (2)
Cs1—O9 ^{iv}	3.134 (2)	N3—O7	1.210 (3)
Cs1—O5 ^v	3.150 (2)	N3—O8	1.275 (3)
Cs1—O7 ^{vi}	3.161 (2)	N3—O9	1.287 (3)
Cs1—O2	3.194 (2)	N3—Cs1 ⁱⁱ	3.657 (2)
Cs1—O6 ^{iv}	3.347 (2)	O7—Cs1 ^x	3.161 (2)
Cs1—O8 ⁱ	3.385 (2)	O7—Cs1 ⁱⁱ	3.624 (2)
Cs1—O4 ^v	3.436 (3)	O8—Cs1 ⁱ	3.385 (2)
Cs1—O3 ^{vii}	3.515 (2)	O9—Cs1 ⁱⁱ	3.134 (2)
Cs1—O2 ^{iv}	3.523 (2)	O9—Cs1 ^{viii}	3.785 (2)
Cs1—O5	3.552 (2)		
O9—Th1—O9 ⁱ	180.0	O2—Cs1—O4 ^v	111.59 (5)
O9—Th1—O5	111.46 (7)	O6 ^{iv} —Cs1—O4 ^v	169.89 (6)
O9 ⁱ —Th1—O5	68.54 (7)	O8 ⁱ —Cs1—O4 ^v	62.74 (5)
O9—Th1—O5 ⁱ	68.54 (7)	O1 ⁱⁱ —Cs1—O3 ^{vii}	103.26 (6)
O9 ⁱ —Th1—O5 ⁱ	111.46 (7)	O4 ⁱⁱⁱ —Cs1—O3 ^{vii}	100.43 (6)
O5—Th1—O5 ⁱ	180.0	O9 ^{iv} —Cs1—O3 ^{vii}	69.90 (5)
O9—Th1—O2	68.05 (7)	O5 ^v —Cs1—O3 ^{vii}	49.34 (5)
O9 ⁱ —Th1—O2	111.95 (7)	O7 ^{vi} —Cs1—O3 ^{vii}	55.17 (6)
O5—Th1—O2	68.25 (7)	O2—Cs1—O3 ^{vii}	160.35 (5)
O5 ⁱ —Th1—O2	111.75 (7)	O6 ^{iv} —Cs1—O3 ^{vii}	116.33 (5)
O9—Th1—O2 ⁱ	111.95 (7)	O8 ⁱ —Cs1—O3 ^{vii}	124.39 (5)
O9 ⁱ —Th1—O2 ⁱ	68.05 (7)	O4 ^v —Cs1—O3 ^{vii}	62.21 (5)
O5—Th1—O2 ⁱ	111.75 (7)	O1 ⁱⁱ —Cs1—O2 ^{iv}	110.03 (6)
O5 ⁱ —Th1—O2 ⁱ	68.25 (7)	O4 ⁱⁱⁱ —Cs1—O2 ^{iv}	62.67 (6)
O2—Th1—O2 ⁱ	180.0	O9 ^{iv} —Cs1—O2 ^{iv}	50.38 (5)
O9—Th1—O3	68.29 (7)	O5 ^v —Cs1—O2 ^{iv}	152.33 (5)
O9 ⁱ —Th1—O3	111.72 (7)	O7 ^{vi} —Cs1—O2 ^{iv}	62.66 (5)
O5—Th1—O3	113.67 (7)	O2—Cs1—O2 ^{iv}	90.06 (4)
O5 ⁱ —Th1—O3	66.33 (7)	O6 ^{iv} —Cs1—O2 ^{iv}	49.46 (5)
O2—Th1—O3	49.78 (7)	O8 ⁱ —Cs1—O2 ^{iv}	104.56 (5)
O2 ⁱ —Th1—O3	130.22 (7)	O4 ^v —Cs1—O2 ^{iv}	120.70 (6)

O9—Th1—O3 ⁱ	111.72 (7)	O3 ^{vii} —Cs1—O2 ^{iv}	109.23 (5)
O9 ⁱ —Th1—O3 ⁱ	68.28 (7)	O1 ⁱⁱ —Cs1—O5	62.42 (6)
O5—Th1—O3 ⁱ	66.33 (7)	O4 ⁱⁱⁱ —Cs1—O5	107.22 (6)
O5 ⁱ —Th1—O3 ⁱ	113.67 (7)	O9 ^{iv} —Cs1—O5	152.10 (5)
O2—Th1—O3 ⁱ	130.22 (7)	O5 ^v —Cs1—O5	64.03 (6)
O2 ⁱ —Th1—O3 ⁱ	49.78 (7)	O7 ^{vi} —Cs1—O5	145.89 (5)
O3—Th1—O3 ⁱ	180.0	O2—Cs1—O5	49.93 (5)
O9—Th1—O8 ⁱ	130.00 (7)	O6 ^{iv} —Cs1—O5	111.39 (5)
O9 ⁱ —Th1—O8 ⁱ	50.00 (7)	O8 ⁱ —Cs1—O5	48.65 (5)
O5—Th1—O8 ⁱ	67.87 (7)	O4 ^v —Cs1—O5	77.61 (6)
O5 ⁱ —Th1—O8 ⁱ	112.13 (7)	O3 ^{vii} —Cs1—O5	111.10 (5)
O2—Th1—O8 ⁱ	66.04 (7)	O2 ^{iv} —Cs1—O5	139.61 (5)
O2 ⁱ —Th1—O8 ⁱ	113.96 (7)	O1—N1—O3	123.0 (3)
O3—Th1—O8 ⁱ	67.52 (7)	O1—N1—O2	121.4 (3)
O3 ⁱ —Th1—O8 ⁱ	112.48 (7)	O3—N1—O2	115.6 (2)
O9—Th1—O8	50.00 (7)	O1—N1—Th1	171.90 (19)
O9 ⁱ —Th1—O8	130.00 (7)	O3—N1—Th1	58.37 (14)
O5—Th1—O8	112.13 (7)	O2—N1—Th1	57.86 (13)
O5 ⁱ —Th1—O8	67.87 (7)	O1—N1—Cs1	80.78 (16)
O2—Th1—O8	113.96 (7)	O3—N1—Cs1	135.65 (16)
O2 ⁱ —Th1—O8	66.04 (7)	O2—N1—Cs1	56.08 (13)
O3—Th1—O8	112.48 (7)	Th1—N1—Cs1	93.18 (6)
O3 ⁱ —Th1—O8	67.52 (7)	N1—O1—Cs1 ^{iv}	151.9 (2)
O8 ⁱ —Th1—O8	180.0	N1—O1—Cs1	80.51 (16)
O9—Th1—O6 ⁱ	114.04 (7)	Cs1 ^{iv} —O1—Cs1	115.37 (7)
O9 ⁱ —Th1—O6 ⁱ	65.96 (7)	N1—O2—Th1	97.02 (15)
O5—Th1—O6 ⁱ	130.17 (7)	N1—O2—Cs1	104.44 (16)
O5 ⁱ —Th1—O6 ⁱ	49.83 (7)	Th1—O2—Cs1	116.83 (7)
O2—Th1—O6 ⁱ	111.92 (7)	N1—O2—Cs1 ⁱⁱ	113.20 (15)
O2 ⁱ —Th1—O6 ⁱ	68.08 (7)	Th1—O2—Cs1 ⁱⁱ	105.02 (7)
O3—Th1—O6 ⁱ	67.62 (7)	Cs1—O2—Cs1 ⁱⁱ	118.46 (6)
O3 ⁱ —Th1—O6 ⁱ	112.38 (7)	N1—O3—Th1	96.77 (16)
O8 ⁱ —Th1—O6 ⁱ	67.90 (7)	N1—O3—Cs1 ^{viii}	127.70 (16)
O8—Th1—O6 ⁱ	112.10 (7)	Th1—O3—Cs1 ^{viii}	109.60 (7)
O9—Th1—O6	65.96 (7)	O4—N2—O6	123.3 (3)
O9 ⁱ —Th1—O6	114.04 (7)	O4—N2—O5	121.3 (2)
O5—Th1—O6	49.83 (7)	O6—N2—O5	115.4 (2)
O5 ⁱ —Th1—O6	130.17 (7)	O4—N2—Th1	169.0 (2)
O2—Th1—O6	68.08 (7)	O6—N2—Th1	58.96 (13)
O2 ⁱ —Th1—O6	111.92 (7)	O5—N2—Th1	57.49 (13)
O3—Th1—O6	112.38 (7)	O4—N2—Cs1 ^v	73.20 (16)
O3 ⁱ —Th1—O6	67.62 (7)	O6—N2—Cs1 ^v	141.44 (17)
O8 ⁱ —Th1—O6	112.11 (7)	O5—N2—Cs1 ^v	60.20 (13)
O8—Th1—O6	67.90 (7)	Th1—N2—Cs1 ^v	98.63 (7)
O6 ⁱ —Th1—O6	180.0	N2—O4—Cs1 ^{ix}	148.2 (2)
O1 ⁱⁱ —Cs1—O4 ⁱⁱⁱ	156.25 (6)	N2—O4—Cs1 ^v	87.06 (17)
O1 ⁱⁱ —Cs1—O9 ^{iv}	89.90 (6)	Cs1 ^{ix} —O4—Cs1 ^v	117.75 (7)
O4 ⁱⁱⁱ —Cs1—O9 ^{iv}	99.74 (6)	N2—O5—Th1	97.33 (15)

O1 ⁱⁱ —Cs1—O5 ^v	93.71 (6)	N2—O5—Cs1 ^v	99.06 (16)
O4 ⁱⁱⁱ —Cs1—O5 ^v	100.55 (6)	Th1—O5—Cs1 ^v	122.56 (8)
O9 ^{iv} —Cs1—O5 ^v	118.27 (5)	N2—O5—Cs1	114.09 (16)
O1 ⁱⁱ —Cs1—O7 ^{vi}	145.66 (6)	Th1—O5—Cs1	106.16 (7)
O4 ⁱⁱⁱ —Cs1—O7 ^{vi}	54.04 (6)	Cs1 ^v —O5—Cs1	115.97 (6)
O9 ^{iv} —Cs1—O7 ^{vi}	58.91 (6)	N2—O6—Th1	96.08 (16)
O5 ^v —Cs1—O7 ^{vi}	89.74 (6)	N2—O6—Cs1 ⁱⁱ	125.14 (16)
O1 ⁱⁱ —Cs1—O2	65.17 (6)	Th1—O6—Cs1 ⁱⁱ	109.54 (7)
O4 ⁱⁱⁱ —Cs1—O2	91.62 (6)	O7—N3—O8	123.3 (3)
O9 ^{iv} —Cs1—O2	123.54 (5)	O7—N3—O9	121.5 (2)
O5 ^v —Cs1—O2	113.40 (5)	O8—N3—O9	115.2 (2)
O7 ^{vi} —Cs1—O2	142.57 (6)	O7—N3—Th1	169.82 (18)
O1 ⁱⁱ —Cs1—O6 ^{iv}	60.69 (6)	O8—N3—Th1	58.82 (13)
O4 ⁱⁱⁱ —Cs1—O6 ^{iv}	109.47 (6)	O9—N3—Th1	57.20 (12)
O9 ^{iv} —Cs1—O6 ^{iv}	50.84 (5)	O7—N3—Cs1 ⁱⁱ	78.86 (16)
O5 ^v —Cs1—O6 ^{iv}	149.23 (6)	O8—N3—Cs1 ⁱⁱ	137.03 (15)
O7 ^{vi} —Cs1—O6 ^{iv}	102.26 (6)	O9—N3—Cs1 ⁱⁱ	56.39 (13)
O2—Cs1—O6 ^{iv}	73.15 (5)	Th1—N3—Cs1 ⁱⁱ	93.37 (6)
O1 ⁱⁱ —Cs1—O8 ⁱ	104.90 (6)	N3—O7—Cs1 ^x	147.48 (19)
O4 ⁱⁱⁱ —Cs1—O8 ⁱ	59.16 (6)	N3—O7—Cs1 ⁱⁱ	82.01 (16)
O9 ^{iv} —Cs1—O8 ⁱ	154.64 (5)	Cs1 ^x —O7—Cs1 ⁱⁱ	126.22 (7)
O5 ^v —Cs1—O8 ⁱ	81.81 (5)	N3—O8—Th1	96.14 (16)
O7 ^{vi} —Cs1—O8 ⁱ	109.40 (6)	N3—O8—Cs1 ⁱ	124.10 (15)
O2—Cs1—O8 ⁱ	50.29 (5)	Th1—O8—Cs1 ⁱ	110.23 (7)
O6 ^{iv} —Cs1—O8 ⁱ	119.24 (5)	N3—O9—Th1	97.60 (15)
O1 ⁱⁱ —Cs1—O4 ^v	129.25 (6)	N3—O9—Cs1 ⁱⁱ	103.60 (16)
O4 ⁱⁱⁱ —Cs1—O4 ^v	62.25 (7)	Th1—O9—Cs1 ⁱⁱ	117.54 (7)
O9 ^{iv} —Cs1—O4 ^v	122.67 (6)	N3—O9—Cs1 ^{viii}	110.88 (15)
O5 ^v —Cs1—O4 ^v	38.31 (6)	Th1—O9—Cs1 ^{viii}	102.81 (7)
O7 ^{vi} —Cs1—O4 ^v	68.42 (6)	Cs1 ⁱⁱ —O9—Cs1 ^{viii}	121.84 (6)

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