

Poly[[triquasesqui- μ_2 -oxalato-terbium(III)] methanol solvate]

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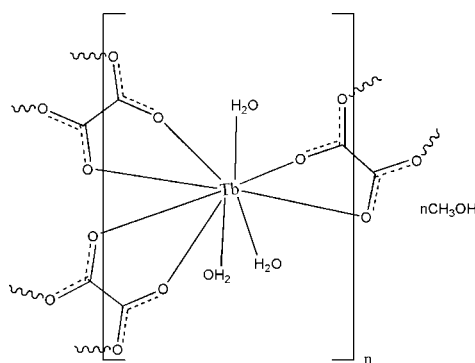
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.022; wR factor = 0.046; data-to-parameter ratio = 14.1.

In the title complex, $\{[\text{Tb}(\text{C}_2\text{O}_4)_{1.5}(\text{H}_2\text{O})_3]\cdot\text{CH}_3\text{OH}\}_n$, each Tb^{III} atom is coordinated by six O atoms from three oxalate ligands and three water molecules, and displays a tricapped-trigonal prismatic geometry. The oxalate groups link the metal ions, forming layers perpendicular to the c axis that can be described *via* topological analysis as a three-connected (6^3) sheet. $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds from the water and methanol molecules to the oxalate ions further interconnect the layers, forming a supramolecular network.

Related literature

For related literature, see: Brandenburg & Putz, (2006); Moulton & Zaworotko (2001); Zeng *et al.*, (2007).



Experimental

Crystal data

 $[\text{Tb}(\text{C}_2\text{O}_4)_{1.5}(\text{H}_2\text{O})_3]\cdot\text{CH}_4\text{O}$ $M_r = 377.04$ Monoclinic, $P2_1/c$ $a = 10.8284$ (2) Å $b = 9.8002$ (2) Å $c = 9.88460$ (10) Å $\beta = 113.7740$ (10)° $V = 959.95$ (3) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 7.41$ mm⁻¹ $T = 296$ (2) K

0.21 × 0.18 × 0.16 mm

Data collection

Bruker APEX-II area-detector

diffractometer

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\text{min}} = 0.231$, $T_{\text{max}} = 0.308$

9378 measured reflections

2196 independent reflections

1901 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.030$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.022$ $wR(F^2) = 0.046$ $S = 1.06$

2196 reflections

156 parameters

9 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.60$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.81$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3W}-\text{H5W}\cdots\text{O1}^{\text{i}}$	0.824 (10)	2.056 (18)	2.823 (4)	155 (4)
$\text{O3W}-\text{H5W}\cdots\text{O3}^{\text{i}}$	0.824 (10)	2.63 (3)	3.048 (4)	113 (3)
$\text{O1W}-\text{H2W}\cdots\text{O2}^{\text{i}}$	0.821 (10)	1.876 (11)	2.685 (4)	168 (4)
$\text{O2W}-\text{H3W}\cdots\text{O6}^{\text{ii}}$	0.825 (10)	2.102 (13)	2.913 (4)	168 (4)
$\text{O2W}-\text{H3W}\cdots\text{O5}^{\text{ii}}$	0.825 (10)	2.64 (3)	3.240 (4)	131 (3)
$\text{O3W}-\text{H6W}\cdots\text{O7}^{\text{iii}}$	0.830 (10)	2.011 (11)	2.841 (4)	176 (4)
$\text{O2W}-\text{H4W}\cdots\text{O7}^{\text{iv}}$	0.825 (10)	1.960 (11)	2.774 (4)	168 (3)
$\text{O1W}-\text{H1W}\cdots\text{O3W}^{\text{iv}}$	0.818 (10)	2.114 (12)	2.906 (4)	163 (3)
$\text{O7}-\text{H7}\cdots\text{O4}^{\text{v}}$	0.82	1.95	2.735 (4)	161

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2004); Diamond (Brandenburg & Putz, 2006); software used to prepare material for publication: SHELXTL.

The authors thank South China Normal University for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2080).

References

- Brandenburg, K. & Putz, H. (2006). DIAMOND. Crystal Impact GbR, Bonn, Germany.
- Bruker (2004). APEX2 (Version 6.12) and SMART (Version 6.12). Bruker AXS Inc, Madison, Wisconsin, USA.
- Moulton, B. & Zaworotko, M. J. (2001). Chem. Rev. **101**, 1629–1658.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). SHELXL97 and SHELXS97. University of Göttingen, Germany.
- Zeng, R.-H., Qiu, Y.-C., Cai, Y.-P., Wu, J.-Z. & Deng, H. (2007). Acta Cryst. E **63**, m1666.

supplementary materials

Acta Cryst. (2007). E63, m2925 [doi:10.1107/S1600536807055043]

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Comment

Molecular self-assembly of supramolecular architectures has received much attention during recent decades (Zeng *et al.*, 2007; Moulton & Zaworotko, 2001). The structures and properties of such systems depend on the coordination and geometric preferences of both the central metal ions and the bridging building blocks, as well as the influence of weaker non-covalent interactions, such as hydrogen bonds and π - π stacking interactions. Recently, we obtained the title coordination polymer, which was synthesized under hydrothermal conditions.

As illustrated in Fig. 1, in the structure of the title compound each Tb^{III} centre is in a tri-capped-trigonal prismatic geometry, defined by six carboxyl O atoms from three oxalate ligands and three water molecules. The oxalate ligands link the Tb^{III} ions to form a smooth layer perpendicular to the *c* axis in which the shortest Tb \cdots Tb separation is 6.210 (3) Å. These layers are connected through O—H \cdots O hydrogen bonding (Table 1) involving the coordinating water and the methanol molecules as donors and acceptors, forming a three-dimensional supramolecular network (Fig. 2). The individual layers formed by the oxalate and metal ions form a motif which, *via* topological analysis, can be described as a 3-connected (6³) sheet (Fig. 3).

Experimental

A mixture of Tb₄O₇ (0.189 g; 0.25 mmol), oxalic acid (0.135 g; 1.5 mmol), water and methanol (3 ml: 7 mL mixture) and HClO₄ (0.385 mmol) was stirred vigorously for 20 min and then sealed in a Teflon-lined stainless-steel autoclave (20 ml, capacity). The autoclave was heated to and maintained at 433 K for 7 days, and then cooled to room temperature at 5 K h⁻¹ to obtain the crystals.

Refinement

Water H atoms were tentatively located in difference Fourier maps and were refined with distance restraints of O—H = 0.82 Å and H \cdots H = 1.29 Å, each within a standard deviation of 0.01 Å; with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O},)$. H atoms on the methanol molecule were placed at calculated positions and were treated as riding on the parent C atoms with C—H = 0.96 Å, and O—H = 0.82 Å, with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O},\text{C})$.

Figures

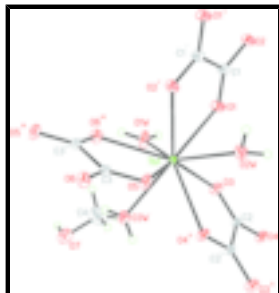


Fig. 1. The structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, 1 - z$; (iii) $1 - x, -y, 1 - z$.

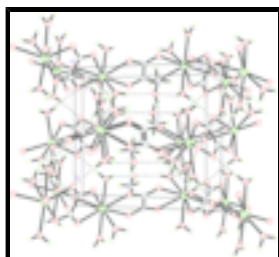


Fig. 2. View of the supramolecular network of the title structure.

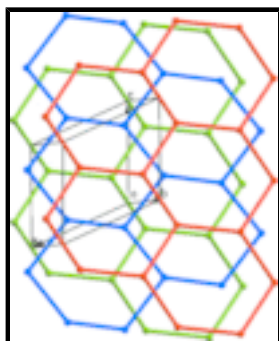


Fig. 3. Illustration of the topological (6^3) motif of the layered structure.

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Crystal data

$[\text{Tb}(\text{C}_2\text{O}_4)_{1.5}(\text{H}_2\text{O})_3] \cdot \text{CH}_4\text{O}$

$M_r = 377.04$

Monoclinic, $P2_1/c$

Hall symbol: $-p\ 2ybc$

$a = 10.8284\ (2)\ \text{\AA}$

$b = 9.8002\ (2)\ \text{\AA}$

$c = 9.88460\ (10)\ \text{\AA}$

$\beta = 113.7740\ (10)^\circ$

$V = 959.95\ (3)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 716$

$D_x = 2.609\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2200 reflections

$\theta = 2.1\text{--}27.5^\circ$

$\mu = 7.41\ \text{mm}^{-1}$

$T = 296\ (2)\ \text{K}$

Blocky, colorless

$0.21 \times 0.18 \times 0.16\ \text{mm}$

Data collection

Bruker APEX-II area-detector diffractometer	2196 independent reflections
Radiation source: fine-focus sealed tube	1901 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.030$
$T = 296(2)$ K	$\theta_{\text{max}} = 27.5^\circ$
φ and ω scan	$\theta_{\text{min}} = 2.1^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -13 \rightarrow 14$
$T_{\text{min}} = 0.231$, $T_{\text{max}} = 0.308$	$k = -12 \rightarrow 10$
9378 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.022$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 0.2004P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
2196 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
156 parameters	$\Delta\rho_{\text{max}} = 0.60 \text{ e } \text{\AA}^{-3}$
9 restraints	$\Delta\rho_{\text{min}} = -0.81 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.0535 (4)	0.0300 (4)	0.5707 (4)	0.0192 (8)
C2	0.4991 (4)	0.0507 (3)	0.5581 (4)	0.0164 (8)
C3	0.0337 (4)	-0.0697 (4)	0.0043 (4)	0.0175 (8)

supplementary materials

C4	0.4073 (6)	0.5977 (6)	0.3276 (6)	0.0630 (16)
H4A	0.4698	0.6234	0.4249	0.094*
H4B	0.4240	0.5050	0.3085	0.094*
H4C	0.3167	0.6058	0.3211	0.094*
O1	0.1573 (3)	0.0771 (3)	0.5630 (3)	0.0253 (6)
O2	0.0265 (3)	0.0275 (3)	0.6839 (3)	0.0234 (6)
O3	0.3887 (2)	0.1093 (3)	0.5326 (3)	0.0235 (6)
O4	0.6077 (3)	0.0669 (3)	0.6689 (3)	0.0219 (6)
O5	0.1274 (3)	-0.1003 (3)	0.1245 (3)	0.0247 (6)
O6	-0.0103 (2)	-0.1420 (3)	-0.1111 (2)	0.0227 (6)
H5W	0.270 (3)	0.2601 (15)	0.180 (4)	0.034*
H2W	0.131 (4)	0.345 (2)	0.325 (3)	0.034*
H1W	0.200 (4)	0.307 (3)	0.4602 (15)	0.034*
H3W	0.150 (2)	-0.219 (4)	0.438 (4)	0.034*
H6W	0.3747 (11)	0.182 (3)	0.223 (4)	0.034*
H4W	0.270 (2)	-0.184 (4)	0.5270 (19)	0.034*
O7	0.4246 (3)	0.6869 (3)	0.2191 (3)	0.0414 (8)
H7	0.4062	0.7655	0.2326	0.062*
O1W	0.1664 (3)	0.2778 (3)	0.3756 (3)	0.0340 (7)
O2W	0.2145 (3)	-0.1722 (3)	0.4416 (3)	0.0316 (7)
O3W	0.2913 (3)	0.1790 (3)	0.1933 (3)	0.0282 (7)
Tb1	0.189510 (16)	0.046207 (17)	0.329650 (15)	0.01138 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.019 (2)	0.016 (2)	0.0237 (18)	-0.0033 (17)	0.0098 (17)	-0.0037 (15)
C2	0.014 (2)	0.015 (2)	0.0195 (17)	0.0010 (17)	0.0060 (15)	0.0049 (14)
C3	0.014 (2)	0.020 (2)	0.0195 (17)	0.0011 (17)	0.0078 (15)	0.0015 (15)
C4	0.083 (5)	0.055 (4)	0.056 (3)	-0.004 (3)	0.033 (3)	-0.012 (3)
O1	0.0203 (16)	0.0317 (17)	0.0262 (13)	-0.0102 (13)	0.0117 (12)	-0.0084 (12)
O2	0.0227 (16)	0.0303 (18)	0.0177 (12)	-0.0068 (13)	0.0087 (12)	-0.0037 (11)
O3	0.0173 (15)	0.0262 (16)	0.0238 (12)	0.0025 (13)	0.0051 (11)	-0.0064 (12)
O4	0.0143 (14)	0.0256 (17)	0.0209 (12)	0.0038 (12)	0.0021 (11)	-0.0023 (11)
O5	0.0224 (16)	0.0263 (16)	0.0178 (12)	0.0075 (13)	0.0004 (11)	-0.0007 (11)
O6	0.0264 (16)	0.0205 (15)	0.0180 (12)	-0.0005 (13)	0.0056 (11)	-0.0048 (11)
O7	0.044 (2)	0.037 (2)	0.0373 (16)	0.0060 (17)	0.0095 (15)	-0.0110 (15)
O1W	0.049 (2)	0.0232 (17)	0.0186 (12)	0.0133 (15)	0.0021 (13)	0.0009 (12)
O2W	0.0266 (17)	0.035 (2)	0.0298 (14)	-0.0039 (15)	0.0079 (13)	0.0091 (13)
O3W	0.0255 (16)	0.0258 (17)	0.0341 (15)	0.0032 (13)	0.0129 (14)	0.0088 (13)
Tb1	0.00966 (10)	0.01277 (11)	0.01034 (8)	-0.00022 (8)	0.00259 (7)	-0.00001 (6)

Geometric parameters (\AA , $^\circ$)

C1—O1	1.246 (4)	O4—Tb1 ⁱⁱ	2.455 (3)
C1—O2	1.266 (4)	O5—Tb1	2.351 (2)
C1—C1 ⁱ	1.529 (7)	O6—Tb1 ⁱⁱⁱ	2.436 (2)
C2—O4	1.252 (4)	O7—H7	0.8200

C2—O3	1.257 (4)	O1W—Tb1	2.348 (3)
C2—C2 ⁱⁱ	1.526 (7)	O1W—H2W	0.821 (10)
C3—O5	1.249 (4)	O1W—H1W	0.818 (10)
C3—O6	1.262 (4)	O2W—Tb1	2.374 (3)
C3—C3 ⁱⁱⁱ	1.535 (7)	O2W—H3W	0.825 (10)
C4—O7	1.453 (6)	O2W—H4W	0.825 (10)
C4—H4A	0.9600	O3W—Tb1	2.434 (3)
C4—H4B	0.9600	O3W—H5W	0.824 (10)
C4—H4C	0.9600	O3W—H6W	0.830 (10)
O1—Tb1	2.486 (2)	Tb1—O2 ⁱ	2.400 (3)
O2—Tb1 ⁱ	2.400 (3)	Tb1—O6 ⁱⁱⁱ	2.436 (2)
O3—Tb1	2.360 (2)	Tb1—O4 ⁱⁱ	2.455 (3)
O1—C1—O2	126.7 (3)	O1W—Tb1—O2W	141.49 (10)
O1—C1—C1 ⁱ	117.2 (4)	O5—Tb1—O2W	77.91 (9)
O2—C1—C1 ⁱ	116.1 (4)	O3—Tb1—O2W	86.94 (10)
O4—C2—O3	126.8 (3)	O1W—Tb1—O2 ⁱ	97.15 (10)
O4—C2—C2 ⁱⁱ	116.6 (4)	O5—Tb1—O2 ⁱ	80.49 (9)
O3—C2—C2 ⁱⁱ	116.5 (4)	O3—Tb1—O2 ⁱ	131.49 (8)
O5—C3—O6	126.2 (3)	O2W—Tb1—O2 ⁱ	71.34 (9)
O5—C3—C3 ⁱⁱⁱ	116.9 (4)	O1W—Tb1—O3W	72.39 (10)
O6—C3—C3 ⁱⁱⁱ	116.8 (4)	O5—Tb1—O3W	83.37 (9)
O7—C4—H4A	109.5	O3—Tb1—O3W	82.42 (9)
O7—C4—H4B	109.5	O2W—Tb1—O3W	138.43 (10)
H4A—C4—H4B	109.5	O2 ⁱ —Tb1—O3W	141.16 (9)
O7—C4—H4C	109.5	O1W—Tb1—O6 ⁱⁱⁱ	71.95 (8)
H4A—C4—H4C	109.5	O5—Tb1—O6 ⁱⁱⁱ	67.79 (8)
H4B—C4—H4C	109.5	O3—Tb1—O6 ⁱⁱⁱ	141.38 (9)
C1—O1—Tb1	118.6 (2)	O2W—Tb1—O6 ⁱⁱⁱ	131.37 (9)
C1—O2—Tb1 ⁱ	121.6 (2)	O2 ⁱ —Tb1—O6 ⁱⁱⁱ	69.88 (8)
C2—O3—Tb1	121.4 (2)	O3W—Tb1—O6 ⁱⁱⁱ	71.32 (9)
C2—O4—Tb1 ⁱⁱ	118.0 (2)	O1W—Tb1—O4 ⁱⁱ	126.88 (10)
C3—O5—Tb1	120.9 (2)	O5—Tb1—O4 ⁱⁱ	70.92 (8)
C3—O6—Tb1 ⁱⁱⁱ	117.4 (2)	O3—Tb1—O4 ⁱⁱ	66.71 (8)
C4—O7—H7	109.5	O2W—Tb1—O4 ⁱⁱ	69.91 (9)
Tb1—O1W—H2W	136 (2)	O2 ⁱ —Tb1—O4 ⁱⁱ	135.56 (9)
Tb1—O1W—H1W	120 (2)	O3W—Tb1—O4 ⁱⁱ	68.96 (9)
H2W—O1W—H1W	104.0 (16)	O6 ⁱⁱⁱ —Tb1—O4 ⁱⁱ	124.77 (8)
Tb1—O2W—H3W	123 (3)	O1W—Tb1—O1	68.74 (9)
Tb1—O2W—H4W	120 (3)	O5—Tb1—O1	140.93 (9)
H3W—O2W—H4W	103.0 (16)	O3—Tb1—O1	66.50 (8)
Tb1—O3W—H5W	116 (3)	O2W—Tb1—O1	73.13 (9)
Tb1—O3W—H6W	120 (3)	O2 ⁱ —Tb1—O1	65.82 (8)
H5W—O3W—H6W	102.2 (16)	O3W—Tb1—O1	135.47 (9)

supplementary materials

O1W—Tb1—O5	137.87 (9)	O6 ⁱⁱⁱ —Tb1—O1	114.59 (8)
O1W—Tb1—O3	73.41 (10)	O4 ⁱⁱ —Tb1—O1	120.61 (8)
O5—Tb1—O3	137.62 (9)		

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x+1, -y, -z+1$; (iii) $-x, -y, -z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3W—H5W \cdots O1 ^{iv}	0.824 (10)	2.056 (18)	2.823 (4)	155 (4)
O3W—H5W \cdots O3 ^{iv}	0.824 (10)	2.63 (3)	3.048 (4)	113 (3)
O1W—H2W \cdots O2 ^{iv}	0.821 (10)	1.876 (11)	2.685 (4)	168 (4)
O2W—H3W \cdots O6 ^v	0.825 (10)	2.102 (13)	2.913 (4)	168 (4)
O2W—H3W \cdots O5 ^v	0.825 (10)	2.64 (3)	3.240 (4)	131 (3)
O3W—H6W \cdots O7 ^{vi}	0.830 (10)	2.011 (11)	2.841 (4)	176 (4)
O2W—H4W \cdots O7 ^{vii}	0.825 (10)	1.960 (11)	2.774 (4)	168 (3)
O1W—H1W \cdots O3W ^{vii}	0.818 (10)	2.114 (12)	2.906 (4)	163 (3)
O7—H7 \cdots O4 ^{viii}	0.82	1.95	2.735 (4)	161

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

Fig. 1

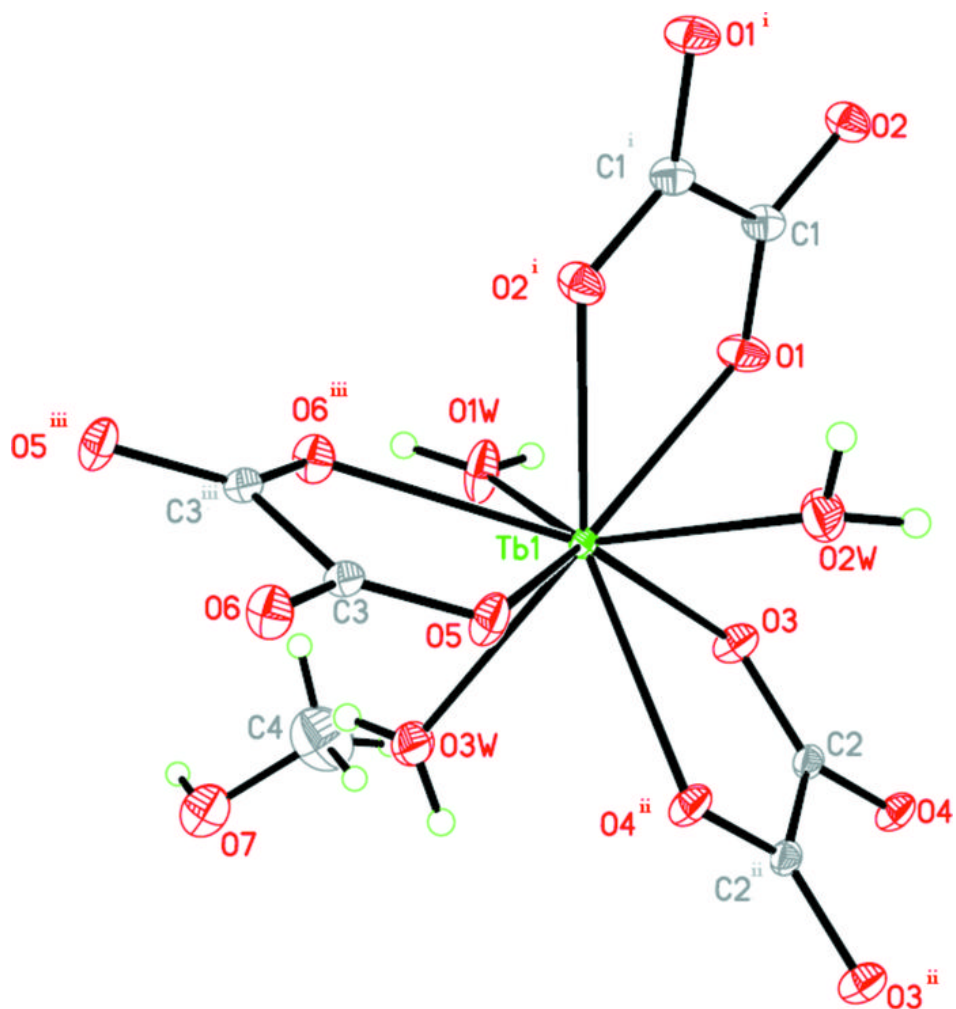


Fig. 2

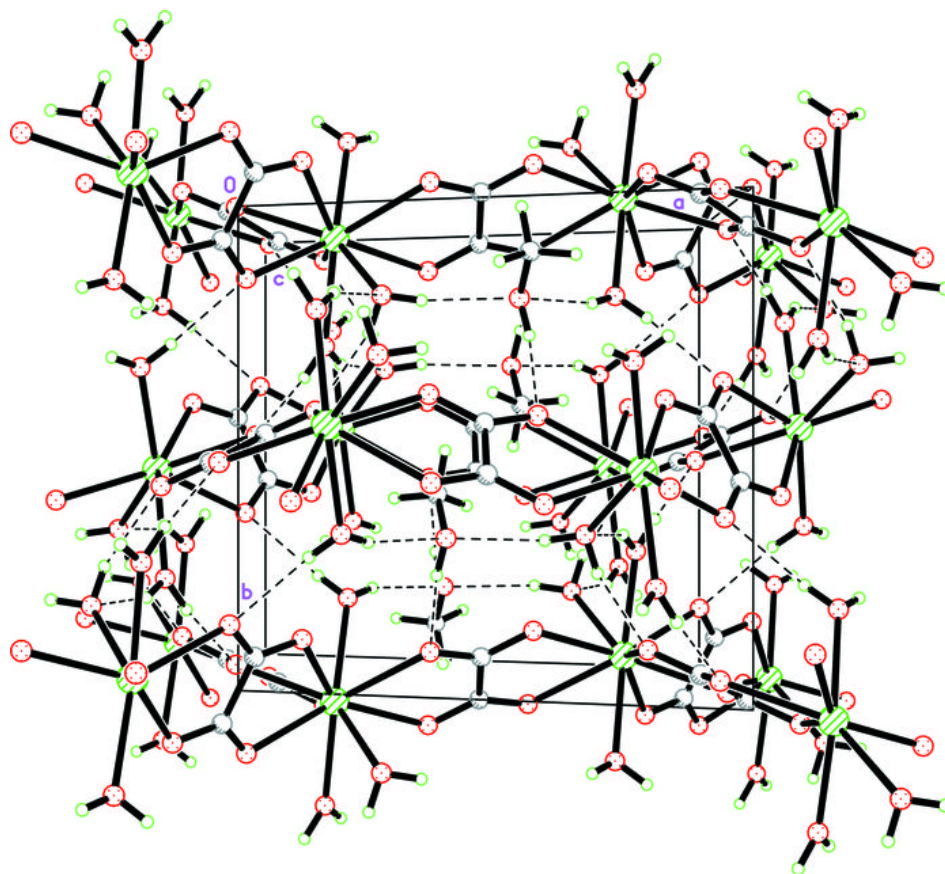


Fig. 3

