

Poly[diaqua- μ_2 -isonicotinato- μ_2 -oxalato-terbium(III)]

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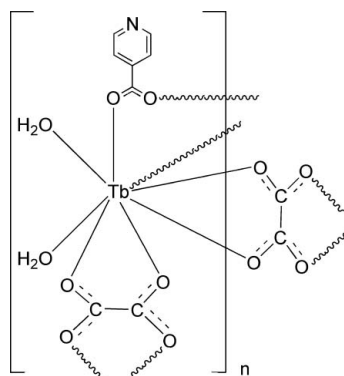
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 Key indicators: single-crystal X-ray study; $T = 273$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.023; wR factor = 0.053; data-to-parameter ratio = 13.1.

In the crystal structure of the title complex, $[\text{Tb}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]_n$, the Tb^{III} cation is coordinated by four O atoms from two oxalate ligands, two O atoms from two isonicotinate ligands and two O atoms from water molecules within a distorted square-antiprismatic coordination. The Tb^{III} cation, the isonicotinate anion and the two crystallographically independent water molecules occupy general positions, whereas one of the two crystallographically independent oxalate anions is located on a center of inversion, and the second oxalate anion is located on a twofold rotation axis. The Tb^{III} cations are linked by the oxalate and isonicotinate anions into layers, which are connected *via* intermolecular hydrogen-bonding and π - π stacking [with centroid-to-centroid distances of 3.509 (2) and 3.343 (3) Å] interactions into a three-dimensional network.

Related literature

For general background on coordination polymers and open-framework materials, see: Yaghi *et al.* (1998, 2003); Serre *et al.* (2004); James (2003). For related structures, see: Xia *et al.* (2004); Feng *et al.* (2003). An independent determination of this structure is reported in the following paper, see: Fang *et al.* (2009).



Experimental

Crystal data

$[\text{Tb}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]$	$V = 2116.95$ (14) Å ³
$M_r = 405.07$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 17.7957$ (6) Å	$\mu = 6.72$ mm ⁻¹
$b = 9.9229$ (4) Å	$T = 273$ (2) K
$c = 12.9673$ (5) Å	$0.36 \times 0.30 \times 0.24$ mm
$\beta = 112.407$ (2)°	

Data collection

Bruker APEXII area-detector diffractometer	7256 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1906 independent reflections
$T_{\text{min}} = 0.113$, $T_{\text{max}} = 0.207$	1618 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	6 restraints
$wR(F^2) = 0.053$	H-atom parameters constrained
$S = 0.91$	$\Delta\rho_{\text{max}} = 0.52$ e Å ⁻³
1906 reflections	$\Delta\rho_{\text{min}} = -0.88$ e Å ⁻³
145 parameters	

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1W}-\text{H1W}\cdots\text{N1}^{\text{i}}$	0.84	1.83	2.665	177
$\text{O1W}-\text{H2W}\cdots\text{O2}^{\text{ii}}$	0.84	2.19	2.992 (3)	159
$\text{O2W}-\text{H3W}\cdots\text{O3}^{\text{iii}}$	0.84	2.00	2.835 (3)	177
$\text{O2W}-\text{H4W}\cdots\text{O1W}^{\text{iv}}$	0.84	2.21	2.998 (3)	156

Symmetry codes: (i) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (ii) $x, -y + 2, z + \frac{1}{2}$; (iii) $-x + 1, -y + 2, -z$; (iv) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z$.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

The authors acknowledge Guang Dong Ocean University for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2122).

References

- Bruker (2004). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Fang, Z.-Q., Zeng, R.-H., Li, Y.-T., Yang, S. & Song, Z.-F. (2009). *Acta Cryst. E* **65**, m118.
- Feng, L. Y., Wang, Y. H., Hu, C. W., Li, Y. G. & Wang, E. B. (2003). *J. Mol. Struct.* **650**, 115–122.
- James, S. L. (2003). *Chem. Soc. Rev.* **32**, 276–288.
- Serre, C., Millange, F., Thouvenot, C., Gardant, N., Pelle, F. & Ferey, G. (2004). *J. Mater. Chem.* **14**, 1540–1543.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Xia, S. Q., Hu, S. M., Dai, J. C., Wu, X. T., Fu, Z. Y., Zhang, J. J. & Du, W. X. (2004). *Polyhedron*, **23**, 1003–1009.
- Yaghi, O. M., O'Keeffe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M. & Kim, J. (2003). *Nature (London)*, **423**, 705–714.
- Yaghi, O. M., Li, H. L., Davis, C., Richardson, D. & Groy, T. L. (1998). *Acc. Chem. Res.* **31**, 474–484.

supplementary materials

Acta Cryst. (2009). E65, m117 [doi:10.1107/S1600536808040518]

Poly[*diaqua- μ_2 -isonicotinato- μ_2 -oxalato-terbium(III)*]

W.-D. Song, S.-J. Li, P.-W. Qin and S.-W. Hu

Comment

The use of multifunctional organic linker molecules in the preparation of coordination polymers and open-framework materials has led to the development of a rich field of chemistry (Yaghi *et al.*, 1998, 2003; Serre *et al.*, 2004; James, 2003) owing to the potential applications of these materials in catalysis, separation, gas storage and molecular recognition. In our own investigations we used isonicotinate and oxalate ligands for the preparation of new coordination polymers, because it has been found that both anions can act as multidentate ligands [Xia *et al.* (2004); Feng *et al.* (2003)] with versatile binding and coordination modes. During these investigations, single crystals of the title compound were obtained.

The Tb^{III} centre in the title compound exhibits a distorted square-antiprismatic coordination geometry, defined by eight O atoms from two oxalate ligands, two O atom from two isonicotinate ligands and two water molecules (Fig. 1). The oxalate and isonicotinate ligands link the Tb^{III} cations with Tb—Tb distances of 6.179 (2) Å, 6.183 (3) Å and 5.045 (2) Å, respectively, thus forming Tb-oxalate-isonicotinate layers with the attached water that is pointing up and down (Fig. 2). The layers are connected into a three-dimensional network *via* inter/intramolecular O—H \cdots O and O—H \cdots N hydrogen bonding interactions (Table 1) involving the coordinated water molecules, the N atoms of isonicotinate and the oxalate O atoms. They are also stabilized by π - π stacking interactions with centroid to centroid distances of 3.509 (2) Å and 3.343 (3) Å, respectively, among parallel pyridinium rings of neighboring complexes.

Experimental

A mixture of Tb₂O₃ (0.5 mmol, 0.175 g), sodium oxalate (1 mmol, 0.134 g), isonicotinic acid (1 mmol, 0.123 g) and H₂O (10 ml) was placed in a 23 ml Teflon reactor, which was heated to 433 K for three days and then cooled to room temperature at a rate of 10 K h⁻¹. The crystals obtained were washed with water and dried in air.

Refinement

C-H H atoms were placed in calculated positions and were treated as riding on the parent C atoms with C—H = 0.93 Å, and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The O-H H atoms were located in difference Fourier maps and were refined with distance restraints of O—H = 0.84 Å and H \cdots H = 1.39 Å, each within a standard deviation of 0.01 Å, and with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$.

Figures

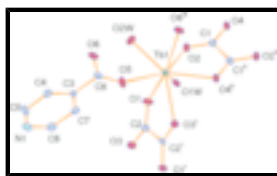


Fig. 1. The structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) 1 - x, y, 0.5 - z; (ii) 0.5 - x, 2.5 - y, -z; (iii) 0.5 - x, 1.5 - y, -z]

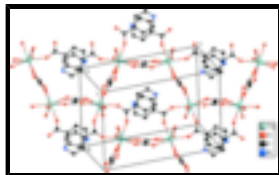


Fig. 2. Crystal structure of the title compound with view onto the layers. The H atoms are not shown for clarity.

Poly[*diaqua-μ₂-isonicotinato-μ₂-oxalato-terbium(III)*]

Crystal data

[Tb(C₆H₄NO₂)(C₂O₄)(H₂O)₂]

$M_r = 405.07$

Monoclinic, *C2/c*

Hall symbol: *-C 2yc*

$a = 17.7957 (6) \text{ \AA}$

$b = 9.9229 (4) \text{ \AA}$

$c = 12.9673 (5) \text{ \AA}$

$\beta = 112.407 (2)^\circ$

$V = 2116.95 (14) \text{ \AA}^3$

$Z = 8$

$F_{000} = 1536$

$D_x = 2.542 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

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

Cell parameters from 8000 reflections

$\theta = 1.7\text{--}26.0^\circ$

$\mu = 6.72 \text{ mm}^{-1}$

$T = 273 (2) \text{ K}$

Block, colorless

$0.36 \times 0.30 \times 0.24 \text{ mm}$

Data collection

Bruker APEXII area-detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 273(2) \text{ K}$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.113$, $T_{\max} = 0.207$

7256 measured reflections

1906 independent reflections

1618 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\text{max}} = 25.2^\circ$

$\theta_{\text{min}} = 2.4^\circ$

$h = -21 \rightarrow 20$

$k = -11 \rightarrow 11$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

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

$wR(F^2) = 0.053$

$S = 0.91$

1906 reflections

145 parameters

6 restraints

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2 + 5.163P]$$

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

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

$\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.88 \text{ e \AA}^{-3}$

Extinction correction: none

Primary atom site location: structure-invariant direct methods

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Tb1	0.323989 (12)	0.96756 (2)	0.074846 (17)	0.01399 (9)
O1	0.46185 (19)	1.0185 (4)	0.1051 (3)	0.0274 (9)
O2	0.3030 (2)	1.1497 (3)	-0.0596 (3)	0.0229 (8)
O5	0.3693 (2)	0.7501 (4)	0.1067 (3)	0.0331 (9)
C1	0.2585 (3)	1.2447 (5)	-0.0542 (4)	0.0172 (11)
C2	0.5146 (3)	1.0111 (5)	0.2013 (4)	0.0172 (11)
C7	0.5237 (3)	0.6498 (6)	0.1361 (4)	0.0231 (12)
H7	0.5190	0.7432	0.1348	0.028*
C8	0.3727 (3)	0.6297 (6)	0.0808 (4)	0.0196 (11)
C3	0.4558 (3)	0.5688 (5)	0.1108 (3)	0.0163 (11)
C6	0.5989 (3)	0.5889 (7)	0.1636 (4)	0.0281 (13)
H6	0.6444	0.6439	0.1807	0.034*
C4	0.4671 (3)	0.4306 (5)	0.1135 (4)	0.0220 (12)
H4	0.4228	0.3731	0.0961	0.026*
C5	0.54429 (8)	0.37835 (15)	0.14206 (11)	0.0281 (13)
H5	0.5508	0.2853	0.1440	0.034*
N1	0.60972 (8)	0.45622 (15)	0.16691 (11)	0.0279 (11)
O3	0.59033 (8)	1.00505 (15)	0.22872 (11)	0.0229 (8)
O4	0.22609 (8)	1.33232 (15)	-0.12763 (11)	0.0232 (8)
O6	0.31250 (8)	0.55572 (15)	0.03267 (11)	0.0301 (9)
O1W	0.25866 (8)	0.87408 (15)	0.19413 (11)	0.0208 (8)
H1W	0.2122	0.9030	0.1852	0.031*
H2W	0.2833	0.8622	0.2630	0.031*
O2W	0.33025 (8)	0.88114 (15)	-0.09693 (11)	0.0286 (9)
H3W	0.3550	0.9157	-0.1341	0.043*
H4W	0.2966	0.8264	-0.1394	0.043*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tb1	0.01048 (13)	0.01587 (15)	0.01480 (12)	0.00208 (11)	0.00389 (9)	0.00099 (11)

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O1	0.0140 (17)	0.047 (3)	0.0180 (17)	-0.0045 (17)	0.0027 (14)	0.0043 (17)
O2	0.0294 (19)	0.023 (2)	0.0202 (17)	0.0082 (17)	0.0143 (15)	0.0022 (16)
O5	0.039 (2)	0.028 (2)	0.039 (2)	0.017 (2)	0.0227 (19)	0.0083 (19)
C1	0.013 (2)	0.019 (3)	0.021 (3)	0.001 (2)	0.007 (2)	0.001 (2)
C2	0.009 (2)	0.017 (3)	0.021 (2)	-0.002 (2)	0.002 (2)	0.000 (2)
C7	0.019 (3)	0.026 (3)	0.022 (3)	-0.004 (2)	0.005 (2)	-0.009 (2)
C8	0.020 (3)	0.030 (3)	0.012 (2)	0.008 (2)	0.008 (2)	0.010 (2)
C3	0.017 (2)	0.024 (3)	0.007 (2)	0.005 (2)	0.0035 (18)	-0.002 (2)
C6	0.016 (3)	0.047 (4)	0.022 (3)	-0.004 (3)	0.008 (2)	-0.006 (3)
C4	0.020 (3)	0.022 (3)	0.023 (3)	-0.002 (2)	0.007 (2)	-0.004 (2)
C5	0.028 (3)	0.026 (3)	0.034 (3)	0.013 (3)	0.016 (2)	0.007 (3)
N1	0.015 (2)	0.046 (4)	0.024 (2)	0.007 (2)	0.0081 (18)	0.003 (2)
O3	0.0175 (18)	0.033 (2)	0.0197 (17)	-0.0024 (16)	0.0089 (14)	0.0018 (15)
O4	0.032 (2)	0.020 (2)	0.0195 (17)	0.0121 (17)	0.0116 (15)	0.0052 (16)
O6	0.0095 (17)	0.050 (3)	0.0259 (18)	0.0005 (18)	0.0013 (14)	0.0006 (18)
O1W	0.0149 (16)	0.028 (2)	0.0201 (16)	0.0064 (16)	0.0076 (14)	0.0074 (16)
O2W	0.040 (2)	0.028 (2)	0.0232 (18)	-0.0068 (19)	0.0179 (17)	-0.0074 (17)

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

Tb1—O5	2.285 (4)	C7—H7	0.9300
Tb1—O6 ⁱ	2.3055 (14)	C8—O6	1.251 (5)
Tb1—O4 ⁱⁱ	2.3814 (14)	C8—C3	1.505 (6)
Tb1—O1	2.386 (3)	C3—C4	1.385 (7)
Tb1—O2W	2.4286 (13)	C6—N1	1.329 (7)
Tb1—O2	2.439 (3)	C6—H6	0.9300
Tb1—O1W	2.4444 (13)	C4—C5	1.380 (5)
Tb1—O3 ⁱⁱⁱ	2.4476 (13)	C4—H4	0.9300
O1—C2	1.245 (6)	C5—N1	1.3306
O2—C1	1.251 (5)	C5—H5	0.9300
O5—C8	1.249 (6)	O3—Tb1 ⁱⁱⁱ	2.4476 (13)
C1—O4	1.255 (5)	O4—Tb1 ⁱⁱ	2.3814 (14)
C1—C1 ⁱⁱ	1.549 (9)	O6—Tb1 ⁱ	2.3055 (14)
C2—O3	1.257 (5)	O1W—H1W	0.8400
C2—C2 ⁱⁱⁱ	1.537 (9)	O1W—H2W	0.8400
C7—C3	1.382 (7)	O2W—H3W	0.8400
C7—C6	1.387 (7)	O2W—H4W	0.8400
O5—Tb1—O6 ⁱ	103.43 (11)	O4—C1—C1 ⁱⁱ	116.8 (5)
O5—Tb1—O4 ⁱⁱ	151.65 (9)	O1—C2—O3	127.1 (4)
O6 ⁱ —Tb1—O4 ⁱⁱ	80.4	O1—C2—C2 ⁱⁱⁱ	117.5 (5)
O5—Tb1—O1	84.30 (13)	O3—C2—C2 ⁱⁱⁱ	115.4 (5)
O6 ⁱ —Tb1—O1	154.26 (9)	C3—C7—C6	118.6 (5)
O4 ⁱⁱ —Tb1—O1	104.49 (10)	C3—C7—H7	120.7
O5—Tb1—O2W	72.32 (10)	C6—C7—H7	120.7
O6 ⁱ —Tb1—O2W	79.4	O5—C8—O6	125.1 (4)
O4 ⁱⁱ —Tb1—O2W	135.3	O5—C8—C3	117.3 (5)

O1—Tb1—O2W	79.74 (9)	O6—C8—C3	117.6 (4)
O5—Tb1—O2	140.94 (11)	C7—C3—C4	117.7 (4)
O6 ⁱ —Tb1—O2	78.63 (9)	C7—C3—C8	120.8 (5)
O4 ⁱⁱ —Tb1—O2	67.37 (8)	C4—C3—C8	121.5 (4)
O1—Tb1—O2	80.13 (11)	N1—C6—C7	123.6 (5)
O2W—Tb1—O2	69.77 (8)	N1—C6—H6	118.2
O5—Tb1—O1W	75.35 (9)	C7—C6—H6	118.2
O6 ⁱ —Tb1—O1W	72.49 (5)	C5—C4—C3	120.0 (4)
O4 ⁱⁱ —Tb1—O1W	79.29 (5)	C5—C4—H4	120.0
O1—Tb1—O1W	133.11 (8)	C3—C4—H4	120.0
O2W—Tb1—O1W	130.20 (6)	N1—C5—C4	122.4 (2)
O2—Tb1—O1W	138.86 (8)	N1—C5—H5	118.8
O5—Tb1—O3 ⁱⁱⁱ	85.32 (10)	C4—C5—H5	118.8
O6 ⁱ —Tb1—O3 ⁱⁱⁱ	137.68 (6)	C6—N1—C5	117.7 (2)
O4 ⁱⁱ —Tb1—O3 ⁱⁱⁱ	74.2	C2—O3—Tb1 ⁱⁱⁱ	118.5 (2)
O1—Tb1—O3 ⁱⁱⁱ	66.61 (8)	C1—O4—Tb1 ⁱⁱ	118.2 (2)
O2W—Tb1—O3 ⁱⁱⁱ	141.3	C8—O6—Tb1 ⁱ	149.8 (3)
O2—Tb1—O3 ⁱⁱⁱ	119.75 (9)	Tb1—O1W—H1W	117.6
O1W—Tb1—O3 ⁱⁱⁱ	69.9	Tb1—O1W—H2W	123.0
C2—O1—Tb1	119.2 (3)	H1W—O1W—H2W	106.4
C1—O2—Tb1	116.5 (3)	Tb1—O2W—H3W	126.8
C8—O5—Tb1	154.8 (3)	Tb1—O2W—H4W	124.0
O2—C1—O4	126.6 (4)	H3W—O2W—H4W	106.6
O2—C1—C1 ⁱⁱ	116.6 (5)		

Symmetry codes: (i) $-x+1/2, -y+3/2, -z$; (ii) $-x+1/2, -y+5/2, -z$; (iii) $-x+1, y, -z+1/2$.

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1W—H1W \cdots N1 ^{iv}	0.84	1.83	2.665	177
O1W—H2W \cdots O2 ^v	0.84	2.19	2.992 (3)	159
O2W—H3W \cdots O3 ^{vi}	0.84	2.00	2.835 (3)	177
O2W—H4W \cdots O1W ⁱ	0.84	2.21	2.998 (3)	156

Symmetry codes: (iv) $x-1/2, y+1/2, z$; (v) $x, -y+2, z+1/2$; (vi) $-x+1, -y+2, -z$; (i) $-x+1/2, -y+3/2, -z$.

Fig. 1

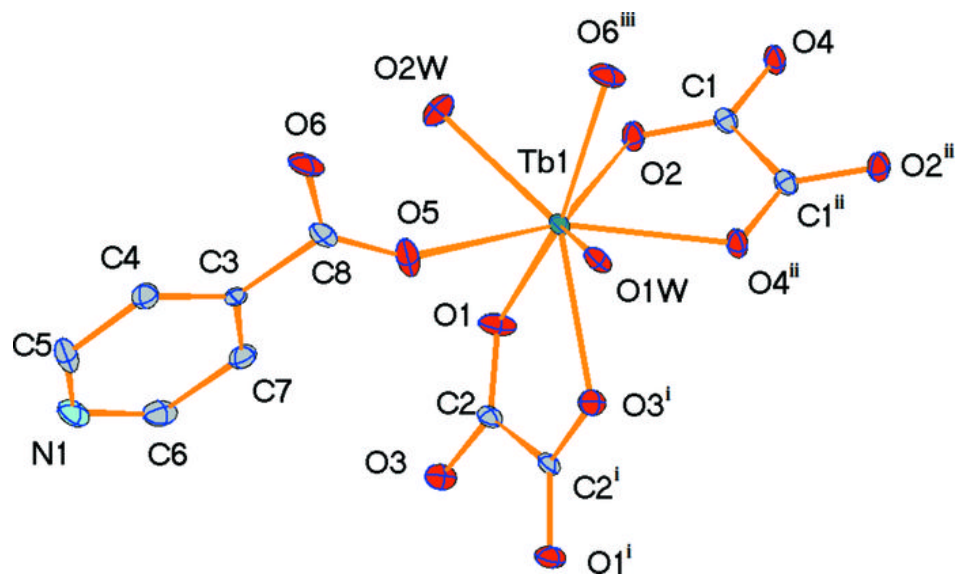


Fig. 2

