metal-organic compounds

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

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In the crystal structure of the title complex, [Tb(C$_6$H$_4$NO$_2$)-(C$_2$O$_4$)(H$_2$O)$_2$]$_n$, the Tb^{III} ion is coordinated by two O atoms from two isonicotinate (inic) anions, four O atoms of two oxalate anions, and two water molecules, displaying a distorted square-antiprismatic geometry. The Tb^{III} ion, the inic anion and the water molecules occupy general positions. One of the two crystallographically independent oxalate anions is located on a center of inversion, whereas the second is located on the twofold rotation axis. The carboxylate groups of the inic and oxalate anions link the terbium metal centres into layers. These layers are connected by O—H···O and N—H···O hydrogen bonding into a three-dimensional network.

Related literature

For background, see: Eddaoudi et al. (2001); Rizk et al. (2005). An independent determination of this structure is reported in the preceeding paper, see: Song et al. (2009).
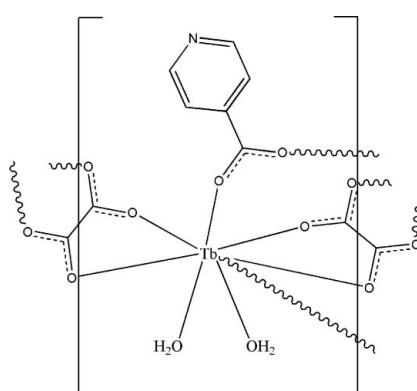
Experimental

Crystal data

[Tb(C$_6$H$_4$NO$_2$)(C$_2$O$_4$)(H$_2$O)$_2$]
M_r = 405.07
Monoclinic, $C2/c$
a = 17.7919 (18) Å
b = 9.9259 (10) Å
c = 12.9670 (13) Å
β = 112.4140 (10)°

V = 2117.0 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 6.72 mm^{-1}
T = 296 (2) K
0.23 × 0.22 × 0.20 mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (APEX2; Bruker, 2004)
T_{min} = 0.241, T_{max} = 0.272

5243 measured reflections
1907 independent reflections
1674 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.063
S = 1.01
1907 reflections
163 parameters

6 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.40 e Å^{-3}
$\Delta\rho_{min}$ = −1.31 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H2W···O3^i	0.84	2.22	2.992 (5)	153
O2W—H4W···O1W^{ii}	0.84	2.19	3.003 (5)	163
O1W—H1W···N1^{iii}	0.84	1.83	2.661 (5)	167
O2W—H3W···O6^{iv}	0.84	2.01	2.836 (5)	172

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

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: PLATON (Spek, 2003) and SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

References

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Rizk, A. T., Kilner, C. A. & Halcrow, M. A. (2005). CrystEngComm, 7, 359–362.
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Song, W.-D., Li, S.-J., Qin, P.-W. & Hu, S.-W. (2009). Acta Cryst. E65, m117.
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supporting information

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

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S1. Comment

The design, synthesis, characterization and properties of coordination networks formed by functionalized organic molecules or anionas as bridges between metal centers are of great interest(Rizk *et al.*, 2005; Eddaoudi *et al.*, 2001). As a building block, isonicotinic acid and oxalic acid are excellent candidates for the construction of such compounds. In our ongoing investigations in this field the title compound was prepared and structurally characterized.

  In the crystal structure of the title compound each Tb^{III} centre is coordinated by six oxygen atoms from two symmetry related inic anions, two crystallographically independent oxalate anions and two crystallographically independent water molecules within a distorted bicapped trigonal prismatic geometry (Fig. 1) . The Tb^{III} ions are linked by the inic and oxalate anions into layers, which are parallel to the b-c-plane (Fig. 2). Tb···Tb separations amount to 6.177 (4) and 5.047 (5) Å, respectively. These layers are connected via O—H···O and N—H···O hydrogen bonding between the water H atoms and the inic and one of the two crystallographically independent oxalate anions into three-dimensional network (Table 1).

S2. Experimental

A mixture of Tb_4O_7 (0.189 g; 0.25 mmol), isonicotinic acid (0.135 g; 1.5 mmol), oxalic acid(0.135 g; 1.5 mmol), water (10 mL) and HNO_3 (0.385 mmol; 0.92g/ml) were stirred for 20 min and then sealed in a 20 mL Teflon-lined stainless-steel autoclave. The autoclave was heated to 433K for 3 days, and then cooled to room temperature at 5 K h⁻¹. By this procedure colorless block-like crystals of the title compound were obtained.

S3. Refinement

The Water H atoms were located in difference Fourier maps, their bond lengths were set to ideal values of O–H = 0.84 and finally they were refined isotropic using a riding model with $U_{iso}(H) = 1.5\ U_{eq}(O)$. C-H H atoms were placed at calculated positions and were treated as riding on the parent C atoms with C—H = 0.93 Å, and with $U_{iso}(H) = 1.2\ U_{eq}(C)$.
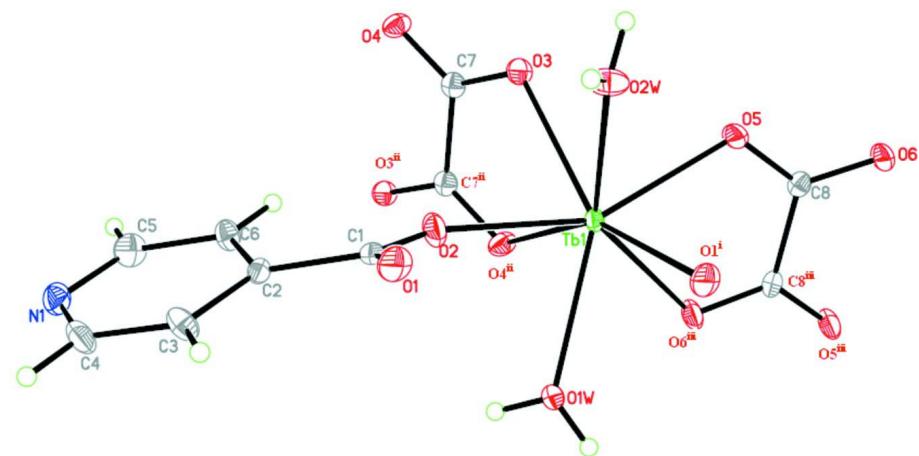
Figure 1

Part of the crystal structure of the title compound with labelling and displacement ellipsoids drawn at the 30% probabbility level. Symmetry codes: (i)1.5-x, 0.5-y, 1-z; (ii)1.5-x, -0.5-y, 1-z; (iii)2-x, y, 1.5-z;
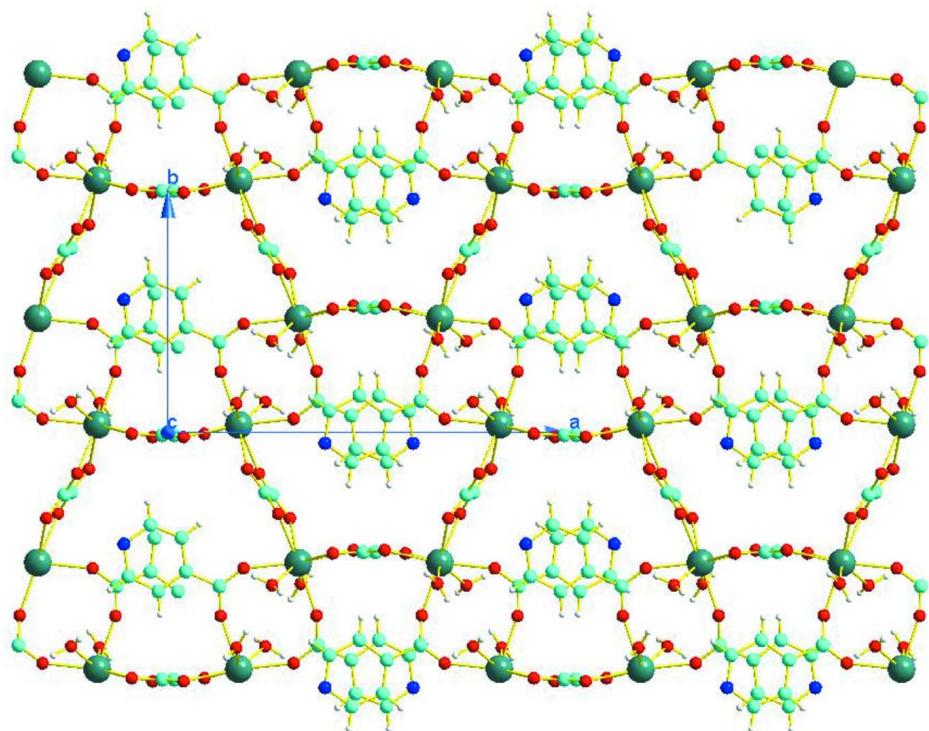
Figure 2

Crystal structure of the title compound with view along the c-axis.

Poly[diaqua-*μ*₂-isonicotinato-*μ*₂-oxalato-terbium(III)]

Crystal data
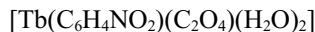
[Tb(C₆H₄NO₂)(C₂O₄)(H₂O)₂]	$F(000) = 1536$
$M_r = 405.07$	$D_x = 2.542$ Mg m⁻³
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 17.7919$ (18) Å	Cell parameters from 2410 reflections
$b = 9.9259$ (10) Å	$\theta = 2.4–27.7°$
$c = 12.9670$ (13) Å	$\mu = 6.72$ mm⁻¹
$\beta = 112.414$ (1)°	$T = 296$ K
$V = 2117.0$ (4) Å³	Block, colourless
$Z = 8$	$0.23 \times 0.22 \times 0.20$ mm

Data collection

Bruker APEXII area-detector diffractometer	1907 independent reflections
Radiation source: fine-focus sealed tube	1674 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.031$
Absorption correction: multi-scan (*APEX2*; Bruker, 2004)	$\theta_{max} = 25.2°$, $\theta_{min} = 2.4°$
$T_{min} = 0.241$, $T_{max} = 0.272$	$h = -21 \rightarrow 20$
5243 measured reflections	$k = -5 \rightarrow 11$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.025$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.063$	
$S = 1.01$	H-atom parameters constrained
1907 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$
163 parameters	where $P = (F_o^2 + 2F_c^2)/3$
6 restraints	$(\Delta/\sigma)_{max} = 0.002$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 1.40$ e Å⁻³
	$\Delta\rho_{min} = -1.31$ e Å⁻³

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.

Refinement. Refinement of F² against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F², conventional R-factors R are based on F, with F set to zero for negative F². The threshold expression of F² > 2sigma(F²) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F² 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Tb1	0.824056 (12)	0.03238 (2)	0.574780 (18)	0.01553 (10)
O5	0.9618 (2)	−0.0185 (4)	0.6050 (3)	0.0289 (9)
O2	0.6877 (2)	0.0558 (4)	0.4672 (3)	0.0326 (9)
O3	0.8029 (2)	−0.1491 (3)	0.4403 (3)	0.0239 (8)
C8	1.0149 (3)	−0.0110 (5)	0.7019 (4)	0.0192 (11)

O6	1.0905 (2)	−0.0055 (4)	0.7291 (3)	0.0272 (9)	
C1	0.6278 (3)	0.1294 (5)	0.4198 (4)	0.0215 (11)	
C2	0.5442 (3)	0.0692 (5)	0.3902 (4)	0.0172 (10)	
C3	0.4756 (3)	0.1501 (6)	0.3627 (4)	0.0264 (12)	
H3	0.4800	0.2434	0.3618	0.032*	
C6	0.5336 (3)	−0.0690 (5)	0.3874 (4)	0.0241 (11)	
H6	0.5781	−0.1263	0.4050	0.029*	
C4	0.4010 (3)	0.0890 (6)	0.3366 (4)	0.0315 (13)	
H4	0.3556	0.1438	0.3206	0.038*	
C5	0.4563 (3)	−0.1211 (5)	0.3584 (5)	0.0314 (13)	
H5	0.4500	−0.2142	0.3564	0.038*	
N1	0.3903 (3)	−0.0438 (5)	0.3330 (4)	0.0309 (11)	
C7	0.7582 (3)	−0.2447 (5)	0.4457 (4)	0.0201 (11)	
O4	0.7261 (2)	−0.3320 (3)	0.3724 (3)	0.0252 (8)	
O1	0.6308 (2)	0.2507 (4)	0.3926 (3)	0.0334 (9)	
O1W	0.75857 (19)	0.1250 (3)	0.6941 (3)	0.0228 (8)	
H1W	0.7146	0.0877	0.6885	0.034*	
H2W	0.7794	0.1546	0.7598	0.034*	
O2W	0.8300 (2)	0.1188 (4)	0.4029 (3)	0.0312 (9)	
H3W	0.8554	0.0794	0.3691	0.047*	
H4W	0.8051	0.1834	0.3631	0.047*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tb1	0.01241 (14)	0.01564 (15)	0.01830 (15)	−0.00225 (9)	0.00558 (10)	−0.00106 (9)
O5	0.0153 (18)	0.048 (2)	0.023 (2)	0.0038 (17)	0.0067 (16)	−0.0063 (18)
O2	0.0144 (18)	0.052 (3)	0.028 (2)	0.0001 (18)	0.0045 (16)	0.001 (2)
O3	0.0271 (19)	0.0201 (18)	0.0287 (19)	−0.0097 (16)	0.0153 (16)	−0.0047 (16)
C8	0.017 (3)	0.018 (2)	0.019 (3)	0.003 (2)	0.003 (2)	0.000 (2)
O6	0.0132 (18)	0.040 (2)	0.027 (2)	0.0019 (16)	0.0068 (16)	−0.0024 (17)
C1	0.019 (3)	0.031 (3)	0.016 (2)	−0.006 (2)	0.009 (2)	−0.007 (2)
C2	0.017 (2)	0.021 (3)	0.014 (2)	−0.005 (2)	0.0058 (19)	0.001 (2)
C3	0.023 (3)	0.028 (3)	0.033 (3)	0.004 (2)	0.017 (2)	0.008 (2)
C6	0.019 (3)	0.022 (3)	0.031 (3)	−0.003 (2)	0.010 (2)	0.001 (2)
C4	0.019 (3)	0.049 (4)	0.030 (3)	0.007 (3)	0.014 (2)	0.008 (3)
C5	0.036 (3)	0.022 (3)	0.040 (3)	−0.013 (3)	0.018 (3)	−0.004 (3)
N1	0.023 (2)	0.044 (3)	0.026 (2)	−0.009 (2)	0.010 (2)	−0.001 (2)
C7	0.019 (2)	0.017 (3)	0.023 (3)	0.004 (2)	0.006 (2)	0.002 (2)
O4	0.033 (2)	0.0225 (18)	0.0218 (18)	−0.0081 (16)	0.0128 (16)	−0.0050 (16)
O1	0.038 (2)	0.027 (2)	0.041 (2)	−0.0189 (18)	0.0211 (19)	−0.0120 (19)
O1W	0.0180 (17)	0.027 (2)	0.0260 (18)	−0.0064 (15)	0.0116 (15)	−0.0071 (16)
O2W	0.049 (2)	0.024 (2)	0.029 (2)	0.0045 (18)	0.0241 (18)	0.0045 (17)

Geometric parameters (Å, º)

Tb1—O1[i]	2.280 (3)	C2—C3	1.389 (7)
Tb1—O2	2.303 (3)	C3—C4	1.379 (7)

Tb1—O5	2.383 (3)	C3—H3	0.9300
Tb1—O4ii	2.385 (3)	C6—C5	1.380 (7)
Tb1—O2W	2.427 (3)	C6—H6	0.9300
Tb1—O3	2.435 (3)	C4—N1	1.330 (8)
Tb1—O6iii	2.443 (4)	C4—H4	0.9300
Tb1—O1W	2.443 (3)	C5—N1	1.335 (7)
O5—C8	1.254 (6)	C5—H5	0.9300
O2—C1	1.244 (6)	C7—O4	1.251 (6)
O3—C7	1.259 (6)	C7—C7ii	1.545 (10)
C8—O6	1.256 (6)	O4—Tb1ii	2.385 (3)
C8—C8iii	1.529 (10)	O1—Tb1i	2.280 (3)
O6—Tb1iii	2.443 (4)	O1W—H1W	0.8429
C1—O1	1.261 (6)	O1W—H2W	0.8420
C1—C2	1.511 (6)	O2W—H3W	0.8367
C2—C6	1.383 (7)	O2W—H4W	0.8365
O1i—Tb1—O2	103.43 (14)	O6—C8—C8iii	116.0 (5)
O1i—Tb1—O5	84.39 (13)	C8—O6—Tb1iii	118.3 (3)
O2—Tb1—O5	154.22 (14)	O2—C1—O1	125.4 (5)
O1i—Tb1—O4ii	151.43 (12)	O2—C1—C2	117.9 (5)
O2—Tb1—O4ii	80.50 (13)	O1—C1—C2	116.7 (5)
O5—Tb1—O4ii	104.46 (13)	C6—C2—C3	118.0 (4)
O1i—Tb1—O2W	72.60 (12)	C6—C2—C1	120.7 (4)
O2—Tb1—O2W	79.21 (13)	C3—C2—C1	121.3 (5)
O5—Tb1—O2W	79.88 (13)	C4—C3—C2	118.6 (5)
O4ii—Tb1—O2W	135.25 (12)	C4—C3—H3	120.7
O1i—Tb1—O3	141.11 (12)	C2—C3—H3	120.7
O2—Tb1—O3	78.56 (13)	C5—C6—C2	119.4 (5)
O5—Tb1—O3	80.16 (12)	C5—C6—H6	120.3
O4ii—Tb1—O3	67.43 (11)	C2—C6—H6	120.3
O2W—Tb1—O3	69.67 (11)	N1—C4—C3	123.8 (5)
O1i—Tb1—O6iii	85.24 (13)	N1—C4—H4	118.1
O2—Tb1—O6iii	137.67 (13)	C3—C4—H4	118.1
O5—Tb1—O6iii	66.65 (12)	N1—C5—C6	122.9 (5)
O4ii—Tb1—O6iii	74.06 (12)	N1—C5—H5	118.6
O2W—Tb1—O6iii	141.48 (12)	C6—C5—H5	118.6
O3—Tb1—O6iii	119.77 (12)	C4—N1—C5	117.4 (4)
O1i—Tb1—O1W	75.34 (12)	O4—C7—O3	126.5 (5)
O2—Tb1—O1W	72.48 (13)	O4—C7—C7ii	117.1 (5)
O5—Tb1—O1W	133.16 (12)	O3—C7—C7ii	116.4 (5)
O4ii—Tb1—O1W	79.12 (11)	C7—O4—Tb1ii	118.1 (3)
O2W—Tb1—O1W	130.27 (12)	C1—O1—Tb1i	154.0 (4)
O3—Tb1—O1W	138.71 (11)	Tb1—O1W—H1W	115.5
O6iii—Tb1—O1W	69.91 (12)	Tb1—O1W—H2W	129.8
C8—O5—Tb1	119.1 (3)	H1W—O1W—H2W	106.0
C1—O2—Tb1	149.9 (4)	Tb1—O2W—H3W	122.5
C7—O3—Tb1	116.5 (3)	Tb1—O2W—H4W	129.8

O5—C8—O6	127.0 (5)	H3W—O2W—H4W	107.4	
O5—C8—C8ⁱⁱⁱ	117.0 (5)			

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H2*W*···O3ⁱᵛ	0.84	2.22	2.992 (5)	153
O2*W*—H4*W*···O1*W*ⁱ	0.84	2.19	3.003 (5)	163
O1*W*—H1*W*···N1ᵛ	0.84	1.83	2.661 (5)	167
O2*W*—H3*W*···O6�vⁱ	0.84	2.01	2.836 (5)	172

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