

**catena-Poly[[diaquaterbium(III)]-tetra-
kis(μ_2 -pyridine-4-carboxylato- κ^2 O:O')-
[diaquaterbium(III)]-bis(μ_2 -pyridine-4-
carboxylato- κ^2 O:O')]**

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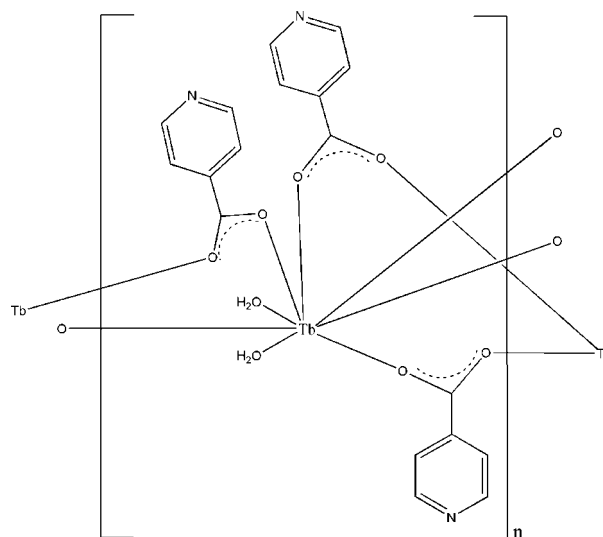
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; disorder in main residue; R factor = 0.035; wR factor = 0.105; data-to-parameter ratio = 15.7.

The title complex, $[\text{Tb}_2(\text{C}_6\text{H}_4\text{NO}_2)_6(\text{H}_2\text{O})_4]_n$, was isolated under hydrothermal conditions using the ligand pyridine-4-carboxylic acid (*HL*) and Tb_2O_3 . The deprotonated L^{2-} ligands adopt bridging coordination modes. The central Tb^{III} atom is bridged by L^{2-} ligands, forming a polymeric chain parallel to the a axis. Supramolecular $\text{O}-\text{H}\cdots\text{N}$ interactions link the chains, building up a layer parallel to (010). $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds also occur. Two of the pyridine rings are disordered by rotation around the central $\text{C}-\text{N}$ direction with occupancy ratios of 0.53 (1):0.47 (1).

Related literature

For the properties of metal-organic coordination polymers, see: Bradshaw *et al.* (2004); Singh & Roesky (2007); Rosi *et al.* (2002); Thirumurugan & Natarajan (2005); Thirumurugan *et al.* (2008); Forster & Cheetham (2002); Fan & Zhu (2007).



Experimental

Crystal data

$[\text{Tb}_2(\text{C}_6\text{H}_4\text{NO}_2)_6(\text{H}_2\text{O})_4]$

$M_r = 1122.52$

Monoclinic, $P2_1/c$

$a = 9.7008$ (10) Å

$b = 19.813$ (2) Å

$c = 11.6253$ (12) Å

$\beta = 112.009$ (1)°

$V = 2071.6$ (4) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 3.46$ mm⁻¹

$T = 293$ K

$0.26 \times 0.20 \times 0.18$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2008a)

$T_{\text{min}} = 0.466$, $T_{\text{max}} = 0.575$

11208 measured reflections

4055 independent reflections

2998 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.105$

$S = 1.11$

4055 reflections

259 parameters

148 restraints

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.78$ e Å⁻³

$\Delta\rho_{\text{min}} = -1.60$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|----------------------------------------------------|--------------|--------------------|-------------|----------------------|
| $\text{O7}-\text{H71}\cdots\text{N3}^{\text{i}}$ | 0.84 | 1.96 | 2.787 (7) | 168 |
| $\text{O7}-\text{H72}\cdots\text{N2}^{\text{ii}}$ | 0.84 | 1.98 | 2.802 (5) | 167 |
| $\text{O8}-\text{H81}\cdots\text{N1}^{\text{iii}}$ | 0.85 | 2.01 | 2.837 (7) | 163 |
| $\text{O8}-\text{H82}\cdots\text{O7}^{\text{iv}}$ | 0.85 | 2.16 | 3.002 (5) | 171 |

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008b); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008b); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

This work was supported by the National Natural Science Foundation of China (grant No. 21001071), the Natural Science Research Program of the Education Department of Henan Province (2010A150018) and the Youth Fund Program of Shangqiu Normal University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2711).

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supplementary materials

Acta Cryst. (2011). E67, m1439-m1440 [doi:10.1107/S1600536811038487]

***catena*-Poly[[diaquaterbium(III)]-tetrakis(μ_2 -pyridine-4-carboxylato- $\kappa^2 O:O'$)-
[diaquaterbium(III)]-bis(μ_2 -pyridine-4-carboxylato- $\kappa^2 O:O'$)]**

X. Zhang and B. Zhai

Comment

Nowadays the connection of metal-organic coordination polymers based on transition metals and multifunctional bridging ligands has proven to be a promising field due to their intriguing and beautiful topologies and potential functions in material chemistry (Singh & Roesky, 2007; Forster & Cheetham, 2002). Great effort has been devoted to prepare such materials (Rosi *et al.*, 2002; Thirumurugan & Natarajan, 2005; Fan & Zhu, 2007; Bradshaw *et al.*, 2004; Thirumurugan *et al.*, 2008), for example, multidentate aromatic polycarboxylic acids including benzene-1,2-dicarboxylate, benzene-1,3-dicarboxylate, benzene-1,4-dicarboxylate, benzene-1,2,3-tricarboxylate, benzene-1,2,4-tricarboxylate, benzene-1,3,5-tricarboxylate and benzene-1,2,4,5-tetracarboxylate have been widely used for the syntheses of coordination polymers of transition metal ions, and the syntheses are mainly through the direct interaction between the metal ions and carboxylate groups to construct one-, two-, and three-dimensional networks in a variety of coordination modes. In general, carboxylate positions, functional groups and ligand conformations are important for syntheses of these hybrid materials. The ligand pyridine-4-carboxylic acid (H_2L) has proven to be a good building block for constructing functional coordination polymers. On the other hand, Tb^{3+} complex is strongly fluorescent, having a large fluorescence quantum yield and very long fluorescence lifetime.

In compound I, each Tb^{III} atom is bonded to six O atoms from six different carboxylates ($Tb-O = 2.424(3)-2.491(4)$ Å) and two water molecules ($Tb-O_w = 2.531(3)-2.559(3)$ Å). The coordination geometry around Tb atom can also be described as a distorted square antiprism with $O-Tb-O$ bond angles ranging from $70.52(11)$ to $147.15(11)^\circ$. Adjacent two Tb centers are connected together via four bridging carboxylates with the $Tb \cdots Tb$ distances of 4.349 Å, which are further extended by other two L^{2-} ligand to generate an infinite chain (Figure 1) which develop parallel to the a axis. All carboxylate groups in (I) adopt bridging modes and the potential N-donor coordination site still remains free.

$O-H \cdots N$ supramolecular interactions link the chain to form layers parallel to the $(0\ 1\ 0)$ plane (Table 1, Fig. 2). There are also $O-H \cdots O$ intramolecular hydrogen bonds within the chains (Table 1).

Experimental

Synthesis of $[TbL_3(H_2O)_2]_n$ (I). A mixture of H_2L (0.3 mmol), Tb_2O_3 (0.1 mmol) and H_2O (15 mL) were placed in a 25 mL Teflon-lined steel vessel and heated to $180^\circ C$ for 5 days, then cooled to room temperature. The resulting colorless block-shaped crystals of (I) were washed several times by water and diethyl ether. Elemental analysis calcd for (I) (%): C, 38.52; H, 2.87; N, 7.49. Found: C, 38.46; H, 2.94; N, 7.45. Selected IR spectra for (I): ν (cm^{-1}) = 3449 s, 1632 s, 1401 m, 745 m.

Refinement

Two of the pyridine rings were disordered by slight rotation around the axial C—N bond. The occupancy factors of the two positions were refined restraining the sum of the occupancy factors to be equal to 1. The values obtained after refinement are 0.47 (1) and 0.53 (1). These values were then fixed and the anisotropic thermal parameters were introduced with EADP restraints (Sheldrick, 2008).

H atoms bound to C atoms were placed geometrically and treated as riding with C-H = 0.93 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$. H atoms of water molecule were located in difference Fourier maps and included in the subsequent refinement using restraints (O-H = 0.85 (1) Å and H···H = 1.40 (2) Å) with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. In the last cycles of refinement they were considered as riding on their parent O atoms.

Figures

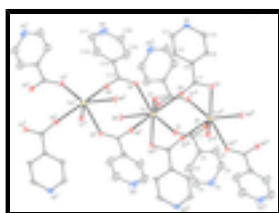


Fig. 1. Partial view of the polymeric chain. Ellipsoids are drawn at the 30% probability level. H atoms and one component of the disordered pyridine rings have been omitted for clarity. [Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$]

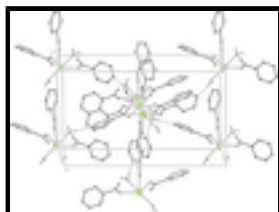


Fig. 2. Partial packing view showing the formation of layer through O-H···N hydrogen bonds. H atoms not involved in hydrogen bondings have been omitted for clarity.

catena-Poly[[diaquaterbium(III)]-tetrakis(μ_2 -pyridine-4-carboxylato- $\kappa^2\text{O}:O'$)-[diaquaterbium(III)]-bis(μ_2 -pyridine-4-carboxylato- $\kappa^2\text{O}:O'$)]

Crystal data

[Tb₂(C₆H₄NO₂)₆(H₂O)₄]

$M_r = 1122.52$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 9.7008$ (10) Å

$b = 19.813$ (2) Å

$c = 11.6253$ (12) Å

$\beta = 112.009$ (1)°

$V = 2071.6$ (4) Å³

$Z = 2$

$F(000) = 1096$

$D_x = 1.800$ Mg m⁻³

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

Cell parameters from 5467 reflections

$\theta = 2.2$ – 26.4 °

$\mu = 3.46$ mm⁻¹

$T = 293$ K

Block, colourless

$0.26 \times 0.20 \times 0.18$ mm

Data collection

| | |
|-------------------------------------------------------------|------------------------------------------------------------------------|
| Bruker SMART CCD area-detector diffractometer | 4055 independent reflections |
| Radiation source: fine-focus sealed tube graphite | 2998 reflections with $I > 2\sigma(I)$ |
| φ and ω scans | $R_{\text{int}} = 0.026$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 2008) | $\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 2.3^\circ$ |
| $T_{\text{min}} = 0.466$, $T_{\text{max}} = 0.575$ | $h = -11 \rightarrow 11$ |
| 11208 measured reflections | $k = -10 \rightarrow 24$ |
| | $l = -14 \rightarrow 14$ |

Refinement

| | |
|---------------------------------|----------------------------------------------------------------|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.035$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.105$ | H-atom parameters constrained |
| $S = 1.11$ | $w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 5.420P]$ |
| 4055 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 259 parameters | $(\Delta/\sigma)_{\text{max}} = 0.012$ |
| 148 restraints | $\Delta\rho_{\text{max}} = 0.78 \text{ e } \text{\AA}^{-3}$ |
| | $\Delta\rho_{\text{min}} = -1.60 \text{ e } \text{\AA}^{-3}$ |

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 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 $F^2 > 2\sigma(F^2)$ 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. The ISOR instruction are used for C16 C16' C17' C5 C5' C15 C15' C18' atoms to insolve their ADP alerts. The instructions of DFIX and DANG are used for H atoms on O7 and O8 water molecules, in order to place H atoms of water molecules in calculated positions as rigiding atoms. The SIMU and DELU instructions against C16 N3 C13 O6 C1 O2 atoms are used for insolveing their ADP alerts. In addition, the disordered C3 C4 C5 C6 and C3' C4' C5' C6' atoms are localized by the diffeere Fourier map, which are treated as disordered part with 0.5 occupancy. Whereas, the C15 C16 C17 C18 and C15' C16' C17' C18' atoms are treated as disordered part with free refinement.

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|---------------|-------------|----------------------------------|-----------|
| Tb1 | 0.28030 (2) | 0.499202 (11) | 0.50935 (2) | 0.01827 (11) | |

supplementary materials

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|------|-------------|--------------|-------------|-------------|------|
| O1 | 0.3953 (4) | 0.61276 (17) | 0.5299 (3) | 0.0248 (8) | |
| O2 | 0.5886 (4) | 0.60949 (17) | 0.4690 (3) | 0.0270 (8) | |
| O3 | 0.3869 (4) | 0.49073 (17) | 0.3515 (3) | 0.0253 (8) | |
| O4 | 0.5557 (4) | 0.49956 (19) | 0.2667 (4) | 0.0324 (10) | |
| O5 | 0.0756 (4) | 0.43450 (17) | 0.3615 (3) | 0.0235 (8) | |
| O6 | -0.1256 (4) | 0.43637 (18) | 0.4071 (3) | 0.0274 (8) | |
| O7 | 0.1132 (4) | 0.57515 (17) | 0.3392 (3) | 0.0262 (8) | |
| H71 | 0.1377 | 0.6148 | 0.3290 | 0.039* | |
| H72 | 0.0602 | 0.5633 | 0.2667 | 0.039* | |
| O8 | 0.1792 (4) | 0.41684 (18) | 0.6284 (3) | 0.0267 (8) | |
| H81 | 0.2344 | 0.3999 | 0.6975 | 0.040* | |
| H82 | 0.0949 | 0.4233 | 0.6325 | 0.040* | |
| N2 | 0.1002 (5) | 0.4546 (3) | -0.1043 (4) | 0.0355 (12) | |
| C1 | 0.5085 (5) | 0.6369 (2) | 0.5182 (4) | 0.0191 (10) | |
| C2 | 0.5552 (6) | 0.7071 (3) | 0.5691 (5) | 0.0263 (11) | |
| C3 | 0.5412 (18) | 0.7272 (6) | 0.6767 (14) | 0.065 (2) | 0.53 |
| H3 | 0.4991 | 0.6988 | 0.7183 | 0.078* | 0.53 |
| C4 | 0.5922 (18) | 0.7922 (6) | 0.7231 (14) | 0.065 (2) | 0.53 |
| H4 | 0.5850 | 0.8049 | 0.7976 | 0.078* | 0.53 |
| N1 | 0.6468 (7) | 0.8341 (3) | 0.6704 (7) | 0.0652 (19) | |
| C5 | 0.6418 (18) | 0.8184 (6) | 0.5577 (13) | 0.065 (2) | 0.53 |
| H5 | 0.6608 | 0.8519 | 0.5093 | 0.078* | 0.53 |
| C6 | 0.6088 (18) | 0.7530 (6) | 0.5098 (14) | 0.065 (2) | 0.53 |
| H6 | 0.6236 | 0.7410 | 0.4379 | 0.078* | 0.53 |
| C3' | 0.4669 (18) | 0.7485 (7) | 0.6043 (18) | 0.065 (2) | 0.47 |
| H3' | 0.3716 | 0.7349 | 0.5949 | 0.078* | 0.47 |
| C4' | 0.5197 (17) | 0.8116 (7) | 0.6545 (18) | 0.065 (2) | 0.47 |
| H4' | 0.4566 | 0.8389 | 0.6778 | 0.078* | 0.47 |
| C5' | 0.7305 (18) | 0.7961 (7) | 0.6254 (18) | 0.065 (2) | 0.47 |
| H5' | 0.8200 | 0.8139 | 0.6273 | 0.078* | 0.47 |
| C6' | 0.6903 (17) | 0.7308 (7) | 0.5758 (18) | 0.065 (2) | 0.47 |
| H6' | 0.7527 | 0.7052 | 0.5490 | 0.078* | 0.47 |
| C7 | 0.4248 (6) | 0.4912 (2) | 0.2593 (5) | 0.0205 (11) | |
| C8 | 0.3085 (5) | 0.4796 (3) | 0.1332 (4) | 0.0201 (10) | |
| C9 | 0.3287 (7) | 0.5057 (3) | 0.0274 (5) | 0.0286 (12) | |
| H9A | 0.4113 | 0.5317 | 0.0344 | 0.034* | |
| C10 | 0.2195 (7) | 0.4908 (3) | -0.0881 (5) | 0.0353 (15) | |
| H10A | 0.2319 | 0.5076 | -0.1583 | 0.042* | |
| C11 | 0.0841 (6) | 0.4311 (3) | -0.0041 (5) | 0.0392 (15) | |
| H11A | 0.0013 | 0.4045 | -0.0146 | 0.047* | |
| C12 | 0.1823 (6) | 0.4436 (3) | 0.1157 (5) | 0.0304 (12) | |
| H12A | 0.1626 | 0.4276 | 0.1832 | 0.037* | |
| C13 | -0.0423 (5) | 0.4099 (2) | 0.3623 (4) | 0.0148 (9) | |
| C14 | -0.0838 (6) | 0.3403 (3) | 0.3060 (5) | 0.0251 (11) | |
| C15 | -0.061 (2) | 0.3205 (7) | 0.2026 (15) | 0.067 (2) | 0.47 |
| H15 | -0.0141 | 0.3488 | 0.1647 | 0.080* | 0.47 |
| C16 | -0.110 (2) | 0.2552 (6) | 0.1541 (16) | 0.067 (2) | 0.47 |
| H16 | -0.1138 | 0.2452 | 0.0748 | 0.080* | 0.47 |
| N3 | -0.1491 (7) | 0.2101 (3) | 0.2112 (6) | 0.0647 (19) | |

| | | | | | |
|------|--------------|------------|-------------|-----------|------|
| C17 | -0.186 (2) | 0.2304 (7) | 0.3059 (16) | 0.067 (2) | 0.47 |
| H17 | -0.2300 | 0.1996 | 0.3416 | 0.080* | 0.47 |
| C18 | -0.1591 (19) | 0.2972 (7) | 0.3543 (17) | 0.067 (2) | 0.47 |
| H18 | -0.1916 | 0.3112 | 0.4162 | 0.080* | 0.47 |
| C15' | 0.0235 (16) | 0.3043 (6) | 0.2749 (17) | 0.067 (2) | 0.53 |
| H15' | 0.1159 | 0.3229 | 0.2870 | 0.080* | 0.53 |
| C16' | -0.0161 (15) | 0.2386 (6) | 0.2247 (17) | 0.067 (2) | 0.53 |
| H16' | 0.0504 | 0.2144 | 0.2003 | 0.080* | 0.53 |
| C17' | -0.2435 (15) | 0.2459 (6) | 0.2278 (17) | 0.067 (2) | 0.53 |
| H17' | -0.3388 | 0.2285 | 0.2064 | 0.080* | 0.53 |
| C18' | -0.2165 (14) | 0.3119 (6) | 0.2774 (17) | 0.067 (2) | 0.53 |
| H18' | -0.2923 | 0.3356 | 0.2901 | 0.080* | 0.53 |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| Tb1 | 0.01824 (16) | 0.01848 (16) | 0.01805 (16) | -0.00263 (9) | 0.00676 (11) | -0.00260 (9) |
| O1 | 0.0188 (17) | 0.0176 (17) | 0.040 (2) | -0.0057 (14) | 0.0135 (16) | -0.0055 (15) |
| O2 | 0.029 (2) | 0.0208 (18) | 0.037 (2) | 0.0011 (16) | 0.0197 (17) | -0.0011 (16) |
| O3 | 0.034 (2) | 0.031 (2) | 0.0143 (17) | -0.0008 (15) | 0.0121 (16) | -0.0015 (14) |
| O4 | 0.0171 (19) | 0.060 (3) | 0.0183 (19) | -0.0084 (17) | 0.0044 (16) | -0.0052 (17) |
| O5 | 0.0218 (18) | 0.0230 (18) | 0.0260 (19) | -0.0100 (15) | 0.0092 (15) | -0.0068 (15) |
| O6 | 0.0246 (18) | 0.0276 (19) | 0.035 (2) | 0.0016 (16) | 0.0164 (17) | -0.0087 (17) |
| O7 | 0.0292 (19) | 0.0203 (18) | 0.0194 (17) | -0.0051 (15) | -0.0019 (15) | 0.0041 (14) |
| O8 | 0.0188 (17) | 0.035 (2) | 0.029 (2) | 0.0054 (15) | 0.0126 (15) | 0.0136 (16) |
| N2 | 0.029 (3) | 0.053 (3) | 0.017 (2) | 0.008 (2) | -0.001 (2) | -0.008 (2) |
| C1 | 0.019 (2) | 0.013 (2) | 0.023 (3) | -0.0017 (19) | 0.004 (2) | 0.0002 (18) |
| C2 | 0.021 (2) | 0.023 (2) | 0.032 (3) | -0.008 (2) | 0.006 (2) | -0.007 (2) |
| C3 | 0.074 (5) | 0.041 (3) | 0.094 (5) | -0.032 (3) | 0.050 (4) | -0.034 (3) |
| C4 | 0.074 (5) | 0.041 (3) | 0.094 (5) | -0.032 (3) | 0.050 (4) | -0.034 (3) |
| N1 | 0.069 (4) | 0.037 (3) | 0.097 (5) | -0.030 (3) | 0.041 (4) | -0.040 (3) |
| C5 | 0.074 (5) | 0.041 (3) | 0.094 (5) | -0.032 (3) | 0.050 (4) | -0.034 (3) |
| C6 | 0.074 (5) | 0.041 (3) | 0.094 (5) | -0.032 (3) | 0.050 (4) | -0.034 (3) |
| C3' | 0.074 (5) | 0.041 (3) | 0.094 (5) | -0.032 (3) | 0.050 (4) | -0.034 (3) |
| C4' | 0.074 (5) | 0.041 (3) | 0.094 (5) | -0.032 (3) | 0.050 (4) | -0.034 (3) |
| C5' | 0.074 (5) | 0.041 (3) | 0.094 (5) | -0.032 (3) | 0.050 (4) | -0.034 (3) |
| C6' | 0.074 (5) | 0.041 (3) | 0.094 (5) | -0.032 (3) | 0.050 (4) | -0.034 (3) |
| C7 | 0.022 (3) | 0.026 (3) | 0.011 (2) | 0.000 (2) | 0.004 (2) | -0.0010 (19) |
| C8 | 0.018 (2) | 0.031 (3) | 0.010 (2) | 0.004 (2) | 0.005 (2) | -0.001 (2) |
| C9 | 0.027 (3) | 0.047 (3) | 0.014 (2) | -0.001 (2) | 0.010 (2) | -0.001 (2) |
| C10 | 0.036 (3) | 0.056 (4) | 0.012 (3) | 0.012 (3) | 0.007 (2) | 0.001 (2) |
| C11 | 0.023 (3) | 0.055 (4) | 0.035 (3) | -0.010 (3) | 0.005 (3) | -0.011 (3) |
| C12 | 0.025 (3) | 0.046 (3) | 0.019 (3) | -0.005 (3) | 0.008 (2) | -0.003 (2) |
| C13 | 0.017 (2) | 0.012 (2) | 0.011 (2) | -0.0018 (18) | 0.0005 (18) | -0.0014 (17) |
| C14 | 0.021 (2) | 0.020 (2) | 0.031 (3) | -0.003 (2) | 0.006 (2) | -0.009 (2) |
| C15 | 0.061 (4) | 0.039 (3) | 0.108 (6) | -0.021 (3) | 0.041 (4) | -0.043 (4) |
| C16 | 0.061 (4) | 0.039 (3) | 0.108 (6) | -0.021 (3) | 0.041 (4) | -0.043 (4) |
| N3 | 0.063 (4) | 0.032 (3) | 0.084 (5) | -0.016 (3) | 0.011 (4) | -0.031 (3) |

supplementary materials

| | | | | | | |
|------|-----------|-----------|-----------|------------|-----------|------------|
| C17 | 0.061 (4) | 0.039 (3) | 0.108 (6) | -0.021 (3) | 0.041 (4) | -0.043 (4) |
| C18 | 0.061 (4) | 0.039 (3) | 0.108 (6) | -0.021 (3) | 0.041 (4) | -0.043 (4) |
| C15' | 0.061 (4) | 0.039 (3) | 0.108 (6) | -0.021 (3) | 0.041 (4) | -0.043 (4) |
| C16' | 0.061 (4) | 0.039 (3) | 0.108 (6) | -0.021 (3) | 0.041 (4) | -0.043 (4) |
| C17' | 0.061 (4) | 0.039 (3) | 0.108 (6) | -0.021 (3) | 0.041 (4) | -0.043 (4) |
| C18' | 0.061 (4) | 0.039 (3) | 0.108 (6) | -0.021 (3) | 0.041 (4) | -0.043 (4) |

Geometric parameters (Å, °)

| | | | |
|------------------------|-------------|------------|------------|
| Tb1—O3 | 2.426 (4) | C6—H6 | 0.9300 |
| Tb1—O6 ⁱ | 2.432 (3) | C3'—C4' | 1.393 (14) |
| Tb1—O5 | 2.446 (3) | C3'—H3' | 0.9300 |
| Tb1—O2 ⁱⁱ | 2.466 (3) | C4'—H4' | 0.9300 |
| Tb1—O1 | 2.483 (3) | C5'—C6' | 1.410 (14) |
| Tb1—O4 ⁱⁱ | 2.491 (4) | C5'—H5' | 0.9300 |
| Tb1—O7 | 2.530 (3) | C6'—H6' | 0.9300 |
| Tb1—O8 | 2.561 (3) | C7—C8 | 1.495 (7) |
| O1—C1 | 1.250 (6) | C8—C12 | 1.365 (7) |
| O2—C1 | 1.249 (5) | C8—C9 | 1.414 (7) |
| O2—Tb1 ⁱⁱ | 2.466 (3) | C9—C10 | 1.395 (8) |
| O3—C7 | 1.258 (6) | C9—H9A | 0.9300 |
| O4—C7 | 1.250 (7) | C10—H10A | 0.9300 |
| O4—Tb1 ⁱⁱ | 2.491 (4) | C11—C12 | 1.383 (7) |
| O5—C13 | 1.247 (6) | C11—H11A | 0.9300 |
| O6—C13 | 1.232 (6) | C12—H12A | 0.9300 |
| O6—Tb1 ⁱ | 2.432 (3) | C13—C14 | 1.513 (6) |
| O7—H71 | 0.8413 | C14—C18' | 1.329 (12) |
| O7—H72 | 0.8403 | C14—C15 | 1.360 (13) |
| O8—H81 | 0.8508 | C14—C18 | 1.374 (14) |
| O8—H82 | 0.8460 | C14—C15' | 1.415 (12) |
| N2—C10 | 1.314 (8) | C15—C16 | 1.421 (14) |
| N2—C11 | 1.316 (8) | C15—H15 | 0.9300 |
| C1—C2 | 1.513 (7) | C16—N3 | 1.252 (14) |
| C2—C3' | 1.356 (13) | C16—H16 | 0.9300 |
| C2—C6 | 1.357 (12) | N3—C17' | 1.230 (12) |
| C2—C6' | 1.367 (13) | N3—C17 | 1.338 (14) |
| C2—C3 | 1.368 (12) | N3—C16' | 1.362 (13) |
| C3—C4 | 1.411 (13) | C17—C18 | 1.423 (14) |
| C3—H3 | 0.9300 | C17—H17 | 0.9300 |
| C4—N1 | 1.261 (12) | C18—H18 | 0.9300 |
| C4—H4 | 0.9300 | C15'—C16' | 1.419 (13) |
| N1—C4' | 1.259 (13) | C15'—H15' | 0.9300 |
| N1—C5 | 1.331 (13) | C16'—H16' | 0.9300 |
| N1—C5' | 1.349 (13) | C17'—C18' | 1.412 (13) |
| C5—C6 | 1.401 (13) | C17'—H17' | 0.9300 |
| C5—H5 | 0.9300 | C18'—H18' | 0.9300 |
| O3—Tb1—O6 ⁱ | 147.12 (12) | C2—C3'—H3' | 120.1 |

| | | | |
|----------------------------------------|-------------|---------------|------------|
| O3—Tb1—O5 | 84.03 (12) | C4'—C3'—H3' | 120.1 |
| O6 ⁱ —Tb1—O5 | 95.50 (12) | N1—C4'—C3' | 124.5 (13) |
| O3—Tb1—O2 ⁱⁱ | 70.56 (12) | N1—C4'—H4' | 117.8 |
| O6 ⁱ —Tb1—O2 ⁱⁱ | 142.13 (12) | C3'—C4'—H4' | 117.8 |
| O5—Tb1—O2 ⁱⁱ | 82.30 (12) | N1—C5'—C6' | 123.8 (12) |
| O3—Tb1—O1 | 80.33 (11) | N1—C5'—H5' | 118.1 |
| O6 ⁱ —Tb1—O1 | 78.94 (12) | C6'—C5'—H5' | 118.1 |
| O5—Tb1—O1 | 139.44 (12) | C2—C6'—C5' | 116.9 (12) |
| O2 ⁱⁱ —Tb1—O1 | 125.85 (13) | C2—C6'—H6' | 121.6 |
| O3—Tb1—O4 ⁱⁱ | 120.33 (13) | C5'—C6'—H6' | 121.6 |
| O6 ⁱ —Tb1—O4 ⁱⁱ | 79.95 (13) | O4—C7—O3 | 123.8 (5) |
| O5—Tb1—O4 ⁱⁱ | 140.54 (12) | O4—C7—C8 | 117.5 (4) |
| O2 ⁱⁱ —Tb1—O4 ⁱⁱ | 78.39 (12) | O3—C7—C8 | 118.7 (5) |
| O1—Tb1—O4 ⁱⁱ | 78.61 (12) | C12—C8—C9 | 118.1 (5) |
| O3—Tb1—O7 | 77.28 (12) | C12—C8—C7 | 122.1 (5) |
| O6 ⁱ —Tb1—O7 | 71.90 (12) | C9—C8—C7 | 119.8 (5) |
| O5—Tb1—O7 | 69.43 (12) | C10—C9—C8 | 117.2 (6) |
| O2 ⁱⁱ —Tb1—O7 | 138.97 (12) | C10—C9—H9A | 121.4 |
| O1—Tb1—O7 | 70.70 (11) | C8—C9—H9A | 121.4 |
| O4 ⁱⁱ —Tb1—O7 | 141.47 (12) | N2—C10—C9 | 124.4 (5) |
| O3—Tb1—O8 | 136.28 (12) | N2—C10—H10A | 117.8 |
| O6 ⁱ —Tb1—O8 | 72.55 (12) | C9—C10—H10A | 117.8 |
| O5—Tb1—O8 | 70.81 (12) | N2—C11—C12 | 124.2 (5) |
| O2 ⁱⁱ —Tb1—O8 | 71.07 (11) | N2—C11—H11A | 117.9 |
| O1—Tb1—O8 | 140.79 (12) | C12—C11—H11A | 117.9 |
| O4 ⁱⁱ —Tb1—O8 | 70.46 (12) | C8—C12—C11 | 118.9 (5) |
| O7—Tb1—O8 | 122.57 (11) | C8—C12—H12A | 120.5 |
| C1—O1—Tb1 | 135.8 (3) | C11—C12—H12A | 120.5 |
| C1—O2—Tb1 ⁱⁱ | 135.9 (3) | O6—C13—O5 | 125.9 (4) |
| C7—O3—Tb1 | 171.2 (4) | O6—C13—C14 | 117.5 (4) |
| C7—O4—Tb1 ⁱⁱ | 107.9 (3) | O5—C13—C14 | 116.7 (4) |
| C13—O5—Tb1 | 134.8 (3) | C18'—C14—C15 | 96.9 (10) |
| C13—O6—Tb1 ⁱ | 173.6 (3) | C18'—C14—C18 | 39.1 (10) |
| Tb1—O7—H71 | 122.2 | C15—C14—C18 | 118.0 (9) |
| Tb1—O7—H72 | 126.1 | C18'—C14—C15' | 117.3 (8) |
| H71—O7—H72 | 102.6 | C15—C14—C15' | 41.4 (9) |
| Tb1—O8—H81 | 122.0 | C18—C14—C15' | 110.2 (9) |
| Tb1—O8—H82 | 120.6 | C18'—C14—C13 | 124.7 (7) |
| H81—O8—H82 | 106.6 | C15—C14—C13 | 122.8 (7) |
| C10—N2—C11 | 117.1 (5) | C18—C14—C13 | 119.0 (7) |
| O2—C1—O1 | 127.3 (5) | C15'—C14—C13 | 117.9 (6) |
| O2—C1—C2 | 115.6 (4) | C14—C15—C16 | 118.1 (13) |
| O1—C1—C2 | 117.1 (4) | C14—C15—H15 | 120.9 |
| C3'—C2—C6 | 98.8 (10) | C16—C15—H15 | 120.9 |
| C3'—C2—C6' | 118.3 (8) | N3—C16—C15 | 124.2 (14) |

supplementary materials

| | | | |
|------------|------------|----------------|------------|
| C6—C2—C6' | 42.0 (9) | N3—C16—H16 | 117.9 |
| C3'—C2—C3 | 42.0 (9) | C15—C16—H16 | 117.9 |
| C6—C2—C3 | 117.2 (8) | C17'—N3—C16 | 93.6 (12) |
| C6'—C2—C3 | 105.6 (10) | C17'—N3—C17 | 41.9 (11) |
| C3'—C2—C1 | 123.0 (7) | C16—N3—C17 | 116.6 (9) |
| C6—C2—C1 | 122.2 (7) | C17'—N3—C16' | 118.1 (9) |
| C6'—C2—C1 | 118.7 (7) | C16—N3—C16' | 46.0 (10) |
| C3—C2—C1 | 120.5 (6) | C17—N3—C16' | 108.1 (10) |
| C2—C3—C4 | 118.3 (11) | N3—C17—C18 | 122.7 (13) |
| C2—C3—H3 | 120.8 | N3—C17—H17 | 118.6 |
| C4—C3—H3 | 120.8 | C18—C17—H17 | 118.6 |
| N1—C4—C3 | 124.6 (12) | C14—C18—C17 | 117.5 (12) |
| N1—C4—H4 | 117.7 | C14—C18—H18 | 121.3 |
| C3—C4—H4 | 117.7 | C17—C18—H18 | 121.3 |
| C4'—N1—C4 | 43.1 (10) | C14—C15'—C16' | 117.1 (11) |
| C4'—N1—C5 | 95.7 (11) | C14—C15'—H15' | 121.4 |
| C4—N1—C5 | 117.2 (8) | C16'—C15'—H15' | 121.4 |
| C4'—N1—C5' | 116.3 (9) | N3—C16'—C15' | 121.7 (11) |
| C4—N1—C5' | 104.1 (10) | N3—C16'—H16' | 119.1 |
| C5—N1—C5' | 44.9 (10) | C15'—C16'—H16' | 119.1 |
| N1—C5—C6 | 121.8 (12) | N3—C17'—C18' | 124.3 (12) |
| N1—C5—H5 | 119.1 | N3—C17'—H17' | 117.9 |
| C6—C5—H5 | 119.1 | C18'—C17'—H17' | 117.9 |
| C2—C6—C5 | 119.5 (11) | C14—C18'—C17' | 120.6 (11) |
| C2—C6—H6 | 120.2 | C14—C18'—H18' | 119.7 |
| C5—C6—H6 | 120.2 | C17'—C18'—H18' | 119.7 |
| C2—C3'—C4' | 119.7 (12) | | |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-------|-------------|-------------|---------------|
| O7—H71 \cdots N3 ⁱⁱⁱ | 0.84 | 1.96 | 2.787 (7) | 168. |
| O7—H72 \cdots N2 ^{iv} | 0.84 | 1.98 | 2.802 (5) | 167. |
| O8—H81 \cdots N1 ^v | 0.85 | 2.01 | 2.837 (7) | 163. |
| O8—H82 \cdots O7 ⁱ | 0.85 | 2.16 | 3.002 (5) | 171. |

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

Fig. 1

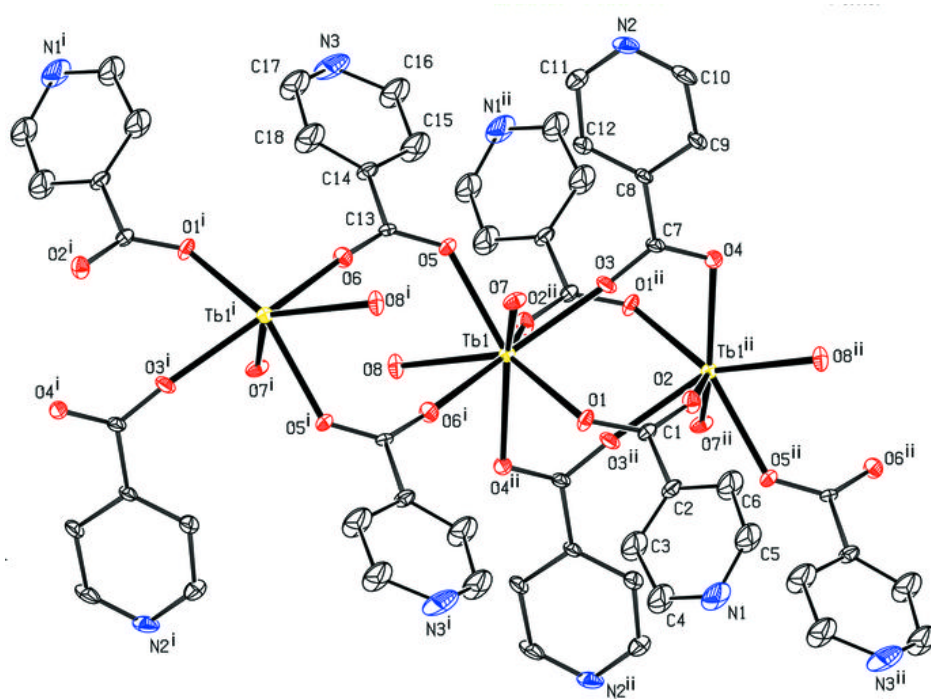


Fig. 2

