

Bis[μ -4-(1*H*-imidazol-3-ium-1-yl)-benzoato- κ^2 O:O']bis[(methanol)tris-(nitrate- κ^2 O,O')]terbium(III)]

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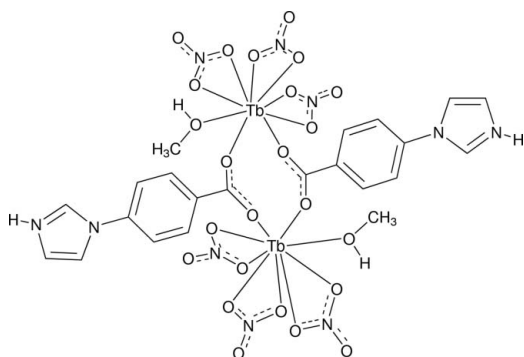
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.026; wR factor = 0.061; data-to-parameter ratio = 16.4.

In the centrosymmetric dinuclear title complex, $[\text{Tb}_2(\text{NO}_3)_6(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_2(\text{CH}_3\text{OH})_2]$, the Tb atoms are bridged by the carboxylate groups of the two 4-(1*H*-imidazol-3-ium-1-yl)-benzoate (iba) ligands. The iba ligand adopts a zwitterionic form with a protonated imidazole group. The Tb atom adopts a distorted tricapped trigonal-prismatic coordination geometry and is coordinated by six O atoms of three chelating nitrate ions, one O atom of the methanol molecule and two O atoms of two iba ligands. The intramolecular Tb...Tb separation is 5.1419 (3) Å. O—H...O and N—H...O hydrogen bonds connect complex molecules into a two-dimensional network.

Related literature

For the preparation of 4-(1*H*-imidazol-1-yl)benzoic acid (iba), see: Zhang *et al.* (2007*a*). To the best of our knowledge, the title compound is the first *f*-block complex of the iba ligand. For *d*-block coordination compounds of the iba ligand, see: Aijaz *et al.* (2009); Bai *et al.* (2009); Gao *et al.* (2008, 2009); Niu *et al.* (2009); Zhang *et al.* (2007*a,b*).



Experimental

Crystal data

$[\text{Tb}_2(\text{NO}_3)_6(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_2(\text{CH}_3\text{O})_2]$
 $M_r = 1130.35$
 Triclinic, $P\bar{1}$
 $a = 8.2966$ (3) Å
 $b = 9.6107$ (3) Å
 $c = 11.6780$ (4) Å
 $\alpha = 95.328$ (2)°
 $\beta = 101.271$ (2)°
 $\gamma = 100.166$ (2)°
 $V = 891.01$ (5) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 4.05$ mm⁻¹
 $T = 296$ K
 $0.32 \times 0.24 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.358$, $T_{\max} = 0.498$
 14627 measured reflections
 4356 independent reflections
 3924 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.061$
 $S = 1.04$
 4356 reflections
 266 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 1.01$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.49$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|---------------------|-----------|---------|-----------|
| Tb1—O2 ⁱ | 2.245 (2) | Tb1—O4 | 2.464 (3) |
| Tb1—O1 | 2.275 (2) | Tb1—O10 | 2.509 (3) |
| Tb1—O12 | 2.385 (3) | Tb1—O7 | 2.529 (3) |
| Tb1—O3 | 2.441 (3) | Tb1—O9 | 2.553 (3) |
| Tb1—O6 | 2.461 (2) | | |

Table 2

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| O12—H1O...O10 ⁱⁱ | 0.81 | 2.15 | 2.960 (4) | 173 |
| N2—H2N...O6 ⁱⁱⁱ | 0.80 (5) | 2.00 (5) | 2.779 (4) | 167 (5) |

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2337).

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supplementary materials

Acta Cryst. (2011). E67, m253-m254 [doi:10.1107/S1600536811002443]

Bis[μ -4-(1*H*-imidazol-3-ium-1-yl)benzoato- κ^2 O:O']bis[(methanol)tris(nitrato- κ^2 O,O')terbium(III)]

Y.-M. Jung and S. W. Lee

Comment

4-(1*H*-Imidazol-1-yl)benzoic acid (iba) is a potential bridging ligand possessing two coordinating groups: a carboxylate group and an imidazole group. This ligand was originally prepared by Chen's group (Zhang *et al.*, 2007*a*). The iba ligand was recently employed to prepare a couple of discrete complexes of *d*-block metals such as Mn (Gao *et al.*, 2008) and Ni (Zhang *et al.*, 2007*b*). It was also utilized for the preparation of coordination polymers of *d*-block metals such as Co (Zhang *et al.*, 2007*a*), Cu (Niu, *et al.*, 2009), Zn (Bai *et al.*, 2009), and Cd (Aijaz *et al.*, 2009; Bai *et al.*, 2009; Gao *et al.*, 2009). By contrast, the corresponding *f*-block complexes, discrete or polymeric, are not known at present. In this context, we attempted to prepare *f*-block coordination polymers by using the iba ligand. Inconsistent with our expectation, however, a discrete molecular species (the title complex) was produced. We herein report the preparation and structure of a terbium complex, the first *f*-block complex of the iba ligand.

The local coordination environment of the Tb^{III} ion in the title complex is presented in Fig. 1, which shows two iba ligands linking two 9-coordinate Tb^{III} ions. The asymmetric unit consists of only half the formula unit, and the other half is generated by crystallographic inversion center. All atoms occupy general positions, and the inversion point is located at the center of the title complex. The imidazole nitrogen (N2) in the iba ligand remains uncoordinated and is protonated. As a result, the iba ligand has a net charge of zero and acts as a zwitterion in which a positive charge is on the imidazole N atom and a negative charge is on the carboxylate group. It would be meaningful to notice that the imidazole N atom is coordinated to the metals in all known *d*-block metal complexes and coordination polymers. Additional coordination of the iba carboxylate group to the metals led to the formation of 2-D or 3-D coordination polymers (Zhang *et al.*, 2007*a*; Niu, *et al.*, 2009; Bai *et al.*, 2009; Aijaz *et al.*, 2009; Bai *et al.*, 2009; Gao *et al.*, 2009). The fact that the N2 atom is not bonded to the Tb^{III} ion in the title complex can probably be explained on the basis of the hard–soft acid–base concept. The hard Tb^{III} ion is expected to have a preference to coordinating to the harder oxygen atom (in the carboxylate group) over the softer nitrogen atom (in the imidazole group).

Each Tb^{III} ion is coordinated to six O atoms from three NO₃[−], one O atom from CH₃OH, and two O atoms from two bis(monodentate) iba ligands. The [TbO₉] core forms a distorted tricapped trigonal prism. Two Tb^{III} ions and two carboxylate groups form a central eight-membered ring. All nitrate ligands act as bidentate ligands. The Tb···Tb separation is 5.1419 (3) Å, which is much longer than the sum (4.0 Å) of van der Waals radii of the two Tb^{III} ions and therefore rules out direct interaction between the two metal ions. The N–H of the imidazole group and O–H of the coordinated methanol molecule participate in the intermolecular hydrogen bonds, which connect the molecules of the title complex into a two-dimensional network (Fig. 2).

Experimental

A mixture of $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (87 mg, 0.2 mmol), 4-(1*H*-imidazol-1-yl)benzoic acid (37 mg, 0.2 mmol), and CH_3OH (6 ml) was heated at 343 K for 24 h in a 23 ml Teflon-lined stainless-steel autoclave and then cooled slowly to room temperature for 24 h. The resulting colorless crystals were collected by filtration, washed by ethanol (5 ml \times 3) and dichloromethane (5 ml \times 3), and then air-dried to give the title complex (82 mg, 0.072 mmol, 37%). mp: 542–544 K. IR (KBr, cm^{-1}): 3889 (w), 3826 (w), 3751 (w), 2912 (*m*), 2628 (*m*), 2364 (*m*), 2069 (*m*), 1792 (*m*), 1591 (*m*), 943 (*m*).

Refinement

The H atom of the methanol OH group was generated in the idealized position [O–H = 0.81 Å, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$] and refined in a riding model approximation. The NH hydrogen atom was located in difference Fourier maps and freely refined. The remaining H atoms were generated in idealized positions (C–H = 0.93–0.96 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

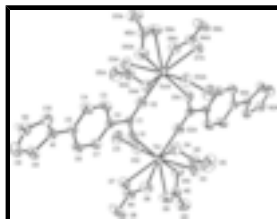


Fig. 1. Molecular structure of the title complex showing 50% probability displacement ellipsoids. Symmetry code for the atoms with A in their labels: $-x + 1, -y + 1, -z + 2$.

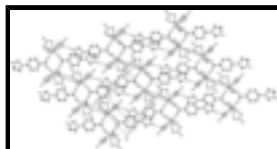


Fig. 2. A two dimensional network formed by N—H...O and O—H...O hydrogen bonds.

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$[\text{Tb}_2(\text{NO}_3)_6(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_2(\text{CH}_4\text{O})_2]$

$M_r = 1130.35$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 8.2966$ (3) Å

$b = 9.6107$ (3) Å

$c = 11.6780$ (4) Å

$\alpha = 95.328$ (2)°

$\beta = 101.271$ (2)°

$\gamma = 100.166$ (2)°

$V = 891.01$ (5) Å³

$Z = 1$

$F(000) = 548$

$D_x = 2.107$ Mg m⁻³

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

Cell parameters from 9939 reflections

$\theta = 2.7$ – 28.5 °

$\mu = 4.05$ mm⁻¹

$T = 296$ K

Block, colourless

$0.32 \times 0.24 \times 0.20$ mm

Data collection

| | |
|---|--|
| Bruker SMART CCD area-detector diffractometer | 4356 independent reflections |
| Radiation source: sealed tube graphite | 3924 reflections with $I > 2\sigma(I)$ |
| φ and ω scans | $R_{\text{int}} = 0.037$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $\theta_{\text{max}} = 28.5^\circ$, $\theta_{\text{min}} = 2.2^\circ$ |
| $T_{\text{min}} = 0.358$, $T_{\text{max}} = 0.498$ | $h = -11 \rightarrow 11$ |
| 14627 measured reflections | $k = -12 \rightarrow 12$ |
| | $l = -15 \rightarrow 15$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.026$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.061$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.04$ | $w = 1/[\sigma^2(F_o^2) + (0.0361P)^2]$ |
| 4356 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 266 parameters | $(\Delta/\sigma)_{\text{max}} = 0.002$ |
| 0 restraints | $\Delta\rho_{\text{max}} = 1.01 \text{ e } \text{\AA}^{-3}$ |
| | $\Delta\rho_{\text{min}} = -0.49 \text{ e } \text{\AA}^{-3}$ |

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 | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|---------------|---------------|----------------------------------|
| Tb1 | 0.457118 (19) | 0.675119 (14) | 0.848450 (11) | 0.03284 (6) |
| O1 | 0.2845 (3) | 0.4704 (2) | 0.8671 (2) | 0.0460 (6) |
| O2 | 0.3792 (4) | 0.3116 (3) | 0.9719 (2) | 0.0512 (6) |
| O3 | 0.7282 (4) | 0.6892 (3) | 0.7935 (3) | 0.0581 (7) |
| O4 | 0.5994 (4) | 0.4789 (3) | 0.8034 (3) | 0.0553 (7) |
| O5 | 0.8288 (6) | 0.5102 (5) | 0.7405 (4) | 0.1010 (14) |

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| | | | | |
|------|-------------|-------------|------------|-------------|
| O6 | 0.3662 (4) | 0.5789 (3) | 0.6383 (2) | 0.0515 (6) |
| O7 | 0.1885 (4) | 0.6835 (3) | 0.7055 (3) | 0.0592 (7) |
| O8 | 0.1450 (6) | 0.6100 (4) | 0.5188 (3) | 0.1017 (15) |
| O9 | 0.4888 (5) | 0.8709 (3) | 0.7163 (2) | 0.0649 (8) |
| O10 | 0.5819 (4) | 0.9363 (3) | 0.9002 (2) | 0.0550 (7) |
| O11 | 0.6051 (5) | 1.0899 (3) | 0.7783 (3) | 0.0784 (10) |
| O12 | 0.2864 (4) | 0.7787 (3) | 0.9605 (2) | 0.0573 (7) |
| H10 | 0.3305 | 0.8559 | 0.9989 | 0.086* |
| N1 | -0.1852 (3) | -0.0986 (3) | 0.5742 (2) | 0.0356 (5) |
| N2 | -0.3091 (5) | -0.3070 (3) | 0.4848 (3) | 0.0497 (8) |
| N3 | 0.7211 (5) | 0.5573 (4) | 0.7785 (3) | 0.0555 (8) |
| N4 | 0.2299 (5) | 0.6250 (3) | 0.6183 (3) | 0.0523 (8) |
| N5 | 0.5595 (4) | 0.9700 (3) | 0.7973 (3) | 0.0472 (7) |
| C1 | 0.2827 (4) | 0.3458 (3) | 0.8879 (3) | 0.0344 (6) |
| C2 | 0.1576 (4) | 0.2281 (3) | 0.8068 (3) | 0.0326 (6) |
| C3 | 0.1500 (5) | 0.0880 (4) | 0.8264 (3) | 0.0488 (9) |
| H3 | 0.2213 | 0.0662 | 0.8912 | 0.059* |
| C4 | 0.0369 (6) | -0.0201 (4) | 0.7502 (3) | 0.0538 (10) |
| H4 | 0.0328 | -0.1145 | 0.7632 | 0.065* |
| C5 | -0.0694 (4) | 0.0123 (3) | 0.6554 (3) | 0.0332 (6) |
| C6 | -0.0660 (5) | 0.1519 (4) | 0.6361 (3) | 0.0446 (8) |
| H6 | -0.1396 | 0.1735 | 0.5724 | 0.054* |
| C7 | 0.0478 (4) | 0.2594 (3) | 0.7121 (3) | 0.0409 (7) |
| H7 | 0.0506 | 0.3538 | 0.6995 | 0.049* |
| C8 | -0.3167 (5) | -0.0831 (4) | 0.4857 (3) | 0.0526 (9) |
| H8 | -0.3467 | 0.0022 | 0.4670 | 0.063* |
| C9 | -0.3922 (5) | -0.2143 (5) | 0.4321 (3) | 0.0554 (10) |
| H9 | -0.4852 | -0.2370 | 0.3698 | 0.066* |
| C10 | -0.1834 (5) | -0.2376 (4) | 0.5700 (3) | 0.0434 (7) |
| H10 | -0.1070 | -0.2784 | 0.6186 | 0.052* |
| C11 | 0.1366 (7) | 0.7167 (6) | 0.9925 (5) | 0.0750 (14) |
| H11A | 0.0994 | 0.7879 | 1.0384 | 0.113* |
| H11B | 0.1569 | 0.6410 | 1.0381 | 0.113* |
| H11C | 0.0518 | 0.6792 | 0.9227 | 0.113* |
| H2N | -0.325 (6) | -0.389 (6) | 0.460 (4) | 0.064 (14)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Tb1 | 0.03738 (9) | 0.02521 (8) | 0.03241 (8) | 0.00405 (6) | 0.00267 (5) | 0.00046 (5) |
| O1 | 0.0431 (14) | 0.0275 (11) | 0.0608 (14) | -0.0002 (10) | 0.0031 (11) | 0.0038 (10) |
| O2 | 0.0586 (17) | 0.0418 (13) | 0.0407 (12) | -0.0013 (12) | -0.0077 (11) | 0.0037 (10) |
| O3 | 0.0486 (16) | 0.0517 (16) | 0.0746 (18) | 0.0049 (13) | 0.0199 (13) | 0.0076 (13) |
| O4 | 0.0537 (17) | 0.0403 (14) | 0.0748 (17) | 0.0140 (13) | 0.0172 (13) | 0.0072 (12) |
| O5 | 0.093 (3) | 0.098 (3) | 0.148 (4) | 0.056 (3) | 0.072 (3) | 0.029 (3) |
| O6 | 0.0658 (18) | 0.0396 (13) | 0.0424 (12) | 0.0117 (12) | 0.0008 (11) | -0.0071 (10) |
| O7 | 0.0545 (17) | 0.0576 (17) | 0.0631 (17) | 0.0208 (14) | -0.0009 (13) | 0.0064 (13) |
| O8 | 0.128 (4) | 0.090 (3) | 0.0587 (19) | 0.019 (3) | -0.045 (2) | 0.0059 (18) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O9 | 0.096 (2) | 0.0408 (14) | 0.0464 (14) | 0.0011 (15) | -0.0020 (14) | 0.0055 (11) |
| O10 | 0.082 (2) | 0.0377 (13) | 0.0405 (12) | 0.0010 (13) | 0.0129 (12) | 0.0018 (10) |
| O11 | 0.105 (3) | 0.0331 (14) | 0.088 (2) | -0.0013 (16) | 0.007 (2) | 0.0200 (14) |
| O12 | 0.0515 (16) | 0.0553 (16) | 0.0598 (15) | 0.0053 (13) | 0.0147 (12) | -0.0152 (12) |
| N1 | 0.0358 (14) | 0.0319 (13) | 0.0357 (12) | 0.0046 (11) | 0.0036 (10) | 0.0007 (10) |
| N2 | 0.058 (2) | 0.0338 (15) | 0.0493 (16) | -0.0016 (14) | 0.0080 (14) | -0.0071 (12) |
| N3 | 0.049 (2) | 0.062 (2) | 0.0601 (19) | 0.0181 (17) | 0.0164 (15) | 0.0073 (16) |
| N4 | 0.063 (2) | 0.0357 (15) | 0.0472 (16) | 0.0061 (15) | -0.0106 (15) | 0.0071 (12) |
| N5 | 0.0543 (19) | 0.0322 (14) | 0.0536 (17) | 0.0057 (13) | 0.0103 (14) | 0.0056 (12) |
| C1 | 0.0349 (16) | 0.0320 (15) | 0.0330 (14) | 0.0000 (12) | 0.0068 (12) | 0.0010 (11) |
| C2 | 0.0350 (16) | 0.0283 (14) | 0.0334 (13) | 0.0037 (12) | 0.0073 (11) | 0.0033 (10) |
| C3 | 0.059 (2) | 0.0328 (16) | 0.0434 (17) | 0.0047 (16) | -0.0126 (15) | 0.0060 (13) |
| C4 | 0.068 (3) | 0.0260 (15) | 0.056 (2) | 0.0059 (16) | -0.0117 (18) | 0.0060 (14) |
| C5 | 0.0344 (16) | 0.0284 (14) | 0.0346 (14) | 0.0049 (12) | 0.0053 (11) | 0.0003 (11) |
| C6 | 0.046 (2) | 0.0334 (16) | 0.0474 (17) | 0.0078 (15) | -0.0082 (14) | 0.0083 (13) |
| C7 | 0.0440 (19) | 0.0258 (14) | 0.0479 (17) | 0.0042 (13) | -0.0005 (14) | 0.0078 (12) |
| C8 | 0.054 (2) | 0.0432 (19) | 0.0512 (19) | 0.0102 (17) | -0.0090 (16) | 0.0002 (15) |
| C9 | 0.051 (2) | 0.055 (2) | 0.0496 (19) | 0.0078 (19) | -0.0028 (16) | -0.0081 (16) |
| C10 | 0.048 (2) | 0.0325 (16) | 0.0457 (17) | 0.0038 (14) | 0.0073 (14) | 0.0013 (13) |
| C11 | 0.064 (3) | 0.089 (4) | 0.078 (3) | 0.014 (3) | 0.034 (2) | 0.004 (3) |

Geometric parameters (Å, °)

| | | | |
|---------------------|-----------|----------|-----------|
| Tb1—O2 ⁱ | 2.245 (2) | N1—C10 | 1.335 (4) |
| Tb1—O1 | 2.275 (2) | N1—C8 | 1.388 (5) |
| Tb1—O12 | 2.385 (3) | N1—C5 | 1.433 (4) |
| Tb1—O3 | 2.441 (3) | N2—C10 | 1.323 (5) |
| Tb1—O6 | 2.461 (2) | N2—C9 | 1.342 (6) |
| Tb1—O4 | 2.464 (3) | N2—H2N | 0.80 (5) |
| Tb1—O10 | 2.509 (3) | C1—C2 | 1.502 (4) |
| Tb1—O7 | 2.529 (3) | C2—C3 | 1.379 (5) |
| Tb1—O9 | 2.553 (3) | C2—C7 | 1.380 (4) |
| Tb1—N3 | 2.855 (3) | C3—C4 | 1.382 (5) |
| Tb1—N4 | 2.910 (3) | C3—H3 | 0.9300 |
| O1—C1 | 1.242 (4) | C4—C5 | 1.371 (5) |
| O2—C1 | 1.248 (4) | C4—H4 | 0.9300 |
| O2—Tb1 ⁱ | 2.245 (2) | C5—C6 | 1.378 (5) |
| O3—N3 | 1.253 (5) | C6—C7 | 1.380 (4) |
| O4—N3 | 1.248 (4) | C6—H6 | 0.9300 |
| O5—N3 | 1.209 (5) | C7—H7 | 0.9300 |
| O6—N4 | 1.274 (5) | C8—C9 | 1.340 (5) |
| O7—N4 | 1.252 (5) | C8—H8 | 0.9300 |
| O8—N4 | 1.216 (4) | C9—H9 | 0.9300 |
| O9—N5 | 1.251 (4) | C10—H10 | 0.9300 |
| O10—N5 | 1.261 (4) | C11—H11A | 0.9600 |
| O11—N5 | 1.203 (4) | C11—H11B | 0.9600 |
| O12—C11 | 1.415 (6) | C11—H11C | 0.9600 |
| O12—H10 | 0.8147 | | |

supplementary materials

| | | | |
|--------------------------|-------------|-------------|------------|
| O2 ⁱ —Tb1—O1 | 93.66 (9) | N5—O10—Tb1 | 98.07 (18) |
| O2 ⁱ —Tb1—O12 | 81.77 (11) | C11—O12—Tb1 | 130.4 (3) |
| O1—Tb1—O12 | 81.94 (10) | C11—O12—H1O | 112.9 |
| O2 ⁱ —Tb1—O3 | 80.85 (11) | Tb1—O12—H1O | 115.1 |
| O1—Tb1—O3 | 125.28 (10) | C10—N1—C8 | 107.5 (3) |
| O12—Tb1—O3 | 148.43 (10) | C10—N1—C5 | 125.2 (3) |
| O2 ⁱ —Tb1—O6 | 152.13 (11) | C8—N1—C5 | 127.3 (3) |
| O1—Tb1—O6 | 81.95 (9) | C10—N2—C9 | 109.9 (3) |
| O12—Tb1—O6 | 124.33 (10) | C10—N2—H2N | 126 (4) |
| O3—Tb1—O6 | 79.46 (10) | C9—N2—H2N | 123 (3) |
| O2 ⁱ —Tb1—O4 | 82.58 (10) | O5—N3—O4 | 122.5 (4) |
| O1—Tb1—O4 | 73.61 (10) | O5—N3—O3 | 120.1 (4) |
| O12—Tb1—O4 | 149.92 (11) | O4—N3—O3 | 117.4 (3) |
| O3—Tb1—O4 | 51.67 (10) | O5—N3—Tb1 | 175.0 (3) |
| O6—Tb1—O4 | 69.74 (9) | O4—N3—Tb1 | 59.30 (18) |
| O2 ⁱ —Tb1—O10 | 76.79 (9) | O3—N3—Tb1 | 58.31 (19) |
| O1—Tb1—O10 | 153.55 (10) | O8—N4—O7 | 122.8 (4) |
| O12—Tb1—O10 | 72.39 (10) | O8—N4—O6 | 120.4 (4) |
| O3—Tb1—O10 | 78.08 (10) | O7—N4—O6 | 116.8 (3) |
| O6—Tb1—O10 | 117.71 (8) | O8—N4—Tb1 | 174.9 (4) |
| O4—Tb1—O10 | 128.09 (10) | O7—N4—Tb1 | 60.03 (17) |
| O2 ⁱ —Tb1—O7 | 154.61 (11) | O6—N4—Tb1 | 57.02 (15) |
| O1—Tb1—O7 | 77.57 (10) | O11—N5—O9 | 122.2 (3) |
| O12—Tb1—O7 | 73.48 (10) | O11—N5—O10 | 121.9 (3) |
| O3—Tb1—O7 | 123.72 (10) | O9—N5—O10 | 115.9 (3) |
| O6—Tb1—O7 | 51.06 (10) | O1—C1—O2 | 124.1 (3) |
| O4—Tb1—O7 | 116.66 (10) | O1—C1—C2 | 118.3 (3) |
| O10—Tb1—O7 | 100.48 (10) | O2—C1—C2 | 117.6 (3) |
| O2 ⁱ —Tb1—O9 | 123.29 (9) | C3—C2—C7 | 119.3 (3) |
| O1—Tb1—O9 | 142.55 (9) | C3—C2—C1 | 120.5 (3) |
| O12—Tb1—O9 | 96.38 (12) | C7—C2—C1 | 120.2 (3) |
| O3—Tb1—O9 | 71.99 (11) | C2—C3—C4 | 120.3 (3) |
| O6—Tb1—O9 | 68.14 (9) | C2—C3—H3 | 119.9 |
| O4—Tb1—O9 | 113.68 (11) | C4—C3—H3 | 119.9 |
| O10—Tb1—O9 | 49.74 (8) | C5—C4—C3 | 119.8 (3) |
| O7—Tb1—O9 | 66.28 (11) | C5—C4—H4 | 120.1 |
| O2 ⁱ —Tb1—N3 | 82.04 (11) | C3—C4—H4 | 120.1 |
| O1—Tb1—N3 | 99.40 (10) | C4—C5—C6 | 120.6 (3) |
| O12—Tb1—N3 | 163.80 (11) | C4—C5—N1 | 120.6 (3) |
| O3—Tb1—N3 | 25.90 (10) | C6—C5—N1 | 118.8 (3) |
| O6—Tb1—N3 | 71.67 (10) | C5—C6—C7 | 119.3 (3) |
| O4—Tb1—N3 | 25.83 (10) | C5—C6—H6 | 120.4 |
| O10—Tb1—N3 | 103.51 (11) | C7—C6—H6 | 120.4 |
| O7—Tb1—N3 | 122.65 (10) | C6—C7—C2 | 120.7 (3) |
| O9—Tb1—N3 | 92.25 (12) | C6—C7—H7 | 119.7 |
| O2 ⁱ —Tb1—N4 | 173.59 (9) | C2—C7—H7 | 119.7 |
| O1—Tb1—N4 | 80.14 (9) | C9—C8—N1 | 107.0 (3) |

| | | | |
|------------------------|-------------|---------------|-----------|
| O12—Tb1—N4 | 98.87 (11) | C9—C8—H8 | 126.5 |
| O3—Tb1—N4 | 101.31 (11) | N1—C8—H8 | 126.5 |
| O6—Tb1—N4 | 25.75 (10) | C8—C9—N2 | 107.6 (3) |
| O4—Tb1—N4 | 94.00 (10) | C8—C9—H9 | 126.2 |
| O10—Tb1—N4 | 109.53 (8) | N2—C9—H9 | 126.2 |
| O7—Tb1—N4 | 25.40 (10) | N2—C10—N1 | 108.0 (3) |
| O9—Tb1—N4 | 63.06 (9) | N2—C10—H10 | 126.0 |
| N3—Tb1—N4 | 97.26 (11) | N1—C10—H10 | 126.0 |
| C1—O1—Tb1 | 143.1 (2) | O12—C11—H11A | 109.5 |
| C1—O2—Tb1 ⁱ | 159.8 (2) | O12—C11—H11B | 109.5 |
| N3—O3—Tb1 | 95.8 (2) | H11A—C11—H11B | 109.5 |
| N3—O4—Tb1 | 94.9 (2) | O12—C11—H11C | 109.5 |
| N4—O6—Tb1 | 97.2 (2) | H11A—C11—H11C | 109.5 |
| N4—O7—Tb1 | 94.6 (2) | H11B—C11—H11C | 109.5 |
| N5—O9—Tb1 | 96.2 (2) | | |

Symmetry codes: (i) $-x+1, -y+1, -z+2$.

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|----------|-------------|-------------|---------------|
| O12—H1O \cdots O10 ⁱⁱ | 0.81 | 2.15 | 2.960 (4) | 173 |
| N2—H2N \cdots O6 ⁱⁱⁱ | 0.80 (5) | 2.00 (5) | 2.779 (4) | 167 (5) |

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

Fig. 1

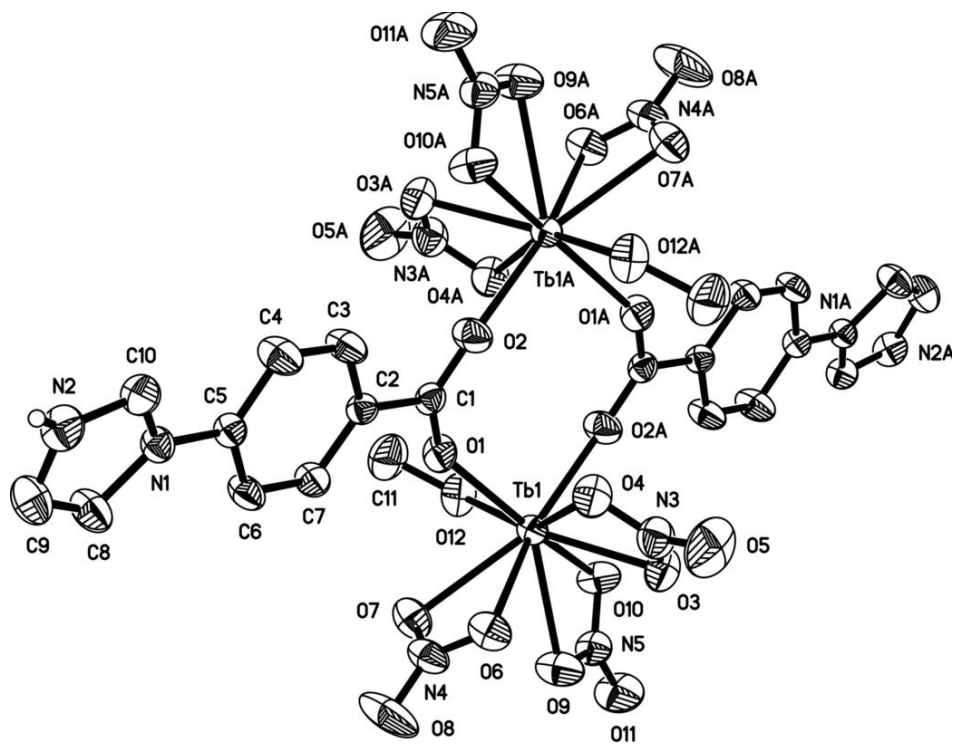


Fig. 2

