



Crystal structure and Hirshfeld surface analysis of tris(acetohydrazide- κ^2N,O)(nitrate- κO)(nitrate- κ^2O,O')terbium(III) nitrate

Chatphorn Theppitak,^a Sakchai Laksee^b and Kittipong Chainok^{a*}

Received 29 December 2021

Accepted 27 February 2022

Edited by C. Schulzke, Universität Greifswald, Germany

Keywords: crystal structure; acetohydrazide; Hirshfeld surface analysis; lanthanide(III) ion; terbium(III).

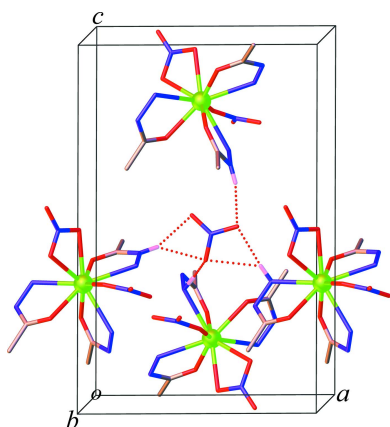
Supporting information: this article has supporting information at journals.iucr.org/e

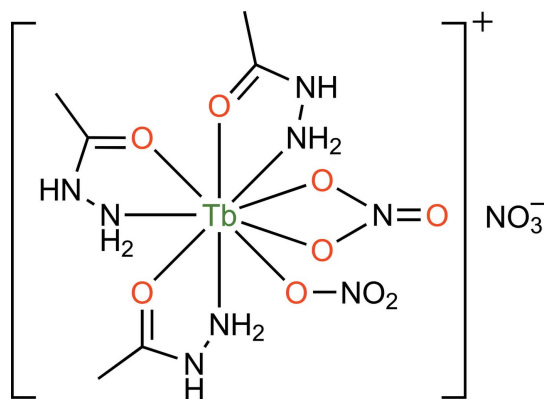
^aThammasat University Research Unit in Multifunctional Crystalline Materials and Applications (TU-McMa), Faculty of Science and Technology, Thammasat University, Khlong Luang, Pathum Thani, 12121, Thailand, and ^bNuclear Technology Research and Development Center, Thailand Institute of Nuclear Technology (Public Organization), Ongkharak, Nakhon Nayok, 26120, Thailand. *Correspondence e-mail: kc@tu.ac.th

In the title lanthanide(III) compound, $[Tb(NO_3)_2(C_2H_6N_2O)_3]NO_3$, the asymmetric unit contains one Tb^{3+} ion, three acetohydrazide ($C_2H_6N_2O$) ligands, two coordinated nitrate anions, and an isolated nitrate anion. The Tb^{3+} ion is in a ninefold coordinated distorted tricapped trigonal–prismatic geometry formed by three oxygen atoms and three nitrogen atoms from three different acetohydrazide ligands and three oxygen atoms from two nitrate anions. In the crystal, the complex molecules and the non-coordinated nitrate anions are assembled into a three-dimensional supramolecular architecture through extensive $N-H\cdots O$ hydrogen-bonding interactions between the amine NH groups of the acetohydrazide ligands and the nitrate oxygen atoms. Hirshfeld surface analysis was performed to aid in the visualization of intermolecular contacts.

1. Chemical context

Over the past two decades, there has been increasing interest in the construction of new lanthanide-based coordination compounds, not only because of their structural diversity but also because of their fascinating potential applications in luminescence, magnetism, adsorption, and similar areas (Roy *et al.*, 2014; Cui *et al.*, 2018; Kuwamura *et al.*, 2021). It is well known that lanthanide(III) ions have a high affinity for and prefer binding to hard donor atoms. Thus, organic ligands with oxygen donor atoms such as aromatic polycarboxylic acids have been used extensively for the formation of these coordination materials (Janicki *et al.*, 2017) whereas organohydrazide ligands have received far less attention. Accordingly, a ConQuest search of the Cambridge Structural Database (CSD, Version 5.42, September 2021 update; Bruno *et al.*, 2002; Groom *et al.*, 2016) reveals only 23 entries for hydrazide-containing lanthanide complexes. Among them, 15 lanthanide coordination complexes have recently been reported by our groups. Some of these complexes exhibited a high CO_2 uptake ability at high pressure (Theppitak *et al.*, 2021a), and have shown great potential as luminescent sensors for acetone and the Co^{2+} ion with good recyclability (Theppitak *et al.*, 2021b). In this work, we present the molecular structure of a new terbium(III) complex, $[Tb(C_2H_6N_2O)_3(NO_3)_2]NO_3$ (**1**), synthesized with acetohydrazide ($C_2H_6N_2O$) as the organic ligand. In addition, a Hirshfeld surface analysis and two-dimensional fingerprint plots were used to quantify the intermolecular contacts in the crystal structure.





2. Structural commentary

The molecular structure of **1** is shown in Fig. 1. The asymmetric unit contains one Tb^{3+} ion, three acetohydrazide ligands, two coordinated nitrate anions, and a non-coordinated nitrate counter-anion. The Tb^{3+} ion is ninefold coordinated (TbN_3O_6) by three nitrogen atoms and three oxygen atoms from three different acetohydrazide ligands, two oxygen atoms from one chelate nitrate anion, and one oxygen atom from another nitrate anion. As can be seen in Fig. 2, the coordination polyhedron of the Tb^{3+} ion is best described as having a distorted tricapped trigonal-prismatic geometry, wherein the N3, N5, O1, O3, O4, and O7 atoms form a trigonal prism, while the N1, O2, and O5 atoms act as caps. The $\text{Tb}-\text{O}$ bond lengths of 2.353 (2)–2.496 (2) Å are slightly shorter than the $\text{Tb}-\text{N}$ bond lengths [2.553 (2)–2.586 (2) Å]. The bond angles around the central Tb^{3+} ion fall into the range of 50.93 (7)–150.97 (7)°. These values are comparable to those reported for

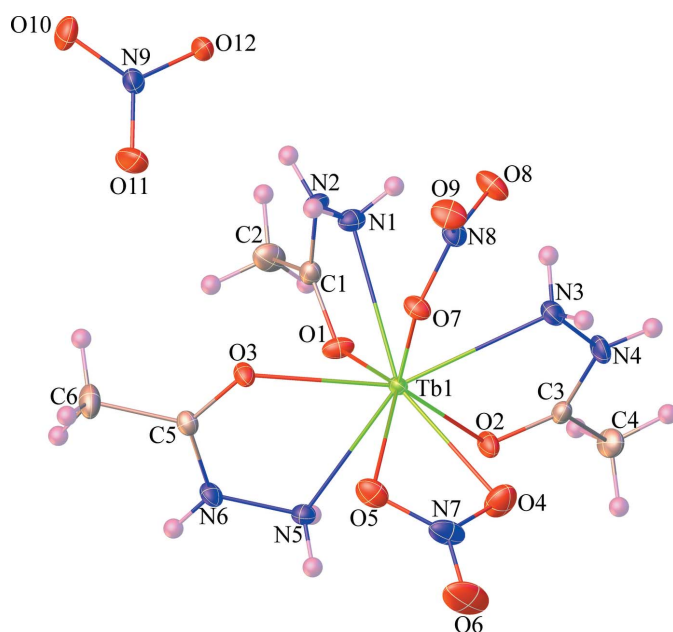


Figure 1
Molecular structure of **1**, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1A \cdots O8	0.84 (2)	2.37 (2)	2.950 (3)	126 (2)
N1–H1B \cdots O10 ⁱ	0.85 (2)	2.36 (2)	3.136 (3)	153 (3)
N2–H2 \cdots O11	0.85 (2)	2.69 (3)	3.070 (3)	109 (2)
N2–H2 \cdots O12	0.85 (2)	2.09 (2)	2.891 (2)	156 (3)
N3–H3A \cdots O8	0.87 (2)	2.46 (3)	2.866 (3)	110 (2)
N3–H3A \cdots O9 ⁱⁱ	0.87 (2)	2.33 (2)	3.146 (3)	157 (2)
N3–H3B \cdots O6 ⁱⁱⁱ	0.85 (2)	2.25 (2)	3.089 (3)	168 (3)
N4–H4 \cdots O10 ^{iv}	0.87 (2)	2.34 (2)	3.102 (3)	147 (3)
N4–H4 \cdots O11 ^{iv}	0.87 (2)	2.17 (2)	2.984 (3)	156 (3)
N5–H5A \cdots O10 ^v	0.86 (2)	2.58 (2)	3.176 (3)	128 (2)
N5–H5A \cdots O12 ^v	0.86 (2)	2.11 (2)	2.964 (2)	173 (3)
N5–H5B \cdots O3 ^{vi}	0.85 (2)	2.51 (2)	3.211 (2)	140 (2)
N6–H6 \cdots O7 ^{vi}	0.85 (2)	2.17 (2)	2.999 (2)	166 (2)
N6–H6 \cdots O10 ^v	0.85 (2)	2.74 (2)	3.170 (3)	114 (2)

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

other ninefold-coordinated Tb^{3+} compounds containing oxygen/nitrogen-donor ligands such as $[\text{Tb}(\text{C}_{17}\text{H}_{13}\text{N}_3)(\text{NO}_3)_2\text{-(DMSO)}]\cdot\text{CH}_3\text{OH}$ (VUKNEW, Chen *et al.*, 2015) and $[\text{Tb}(\text{C}_{13}\text{H}_{22}\text{N}_3)(\text{NO}_3)_3]\cdot\text{MeCN}$ (SEZTOJ, Long *et al.*, 2018).

3. Supramolecular features

Extensive hydrogen-bonding interactions involving the three components of the hydrazide group of the acetohydrazide ligand and the coordinated and non-coordinated nitrate ions contribute to the stabilization of the supramolecular structure of **1** (Table 1; the N–H distances are all fixed with N–H = 0.86 ± 0.02 Å). A closer inspection of the structure reveals that the $[\text{Tb}(\text{C}_2\text{H}_6\text{N}_2\text{O})_3(\text{NO}_3)_2]^+$ complex molecules form centrosymmetric dimers *via* pairs of symmetry-related N3–

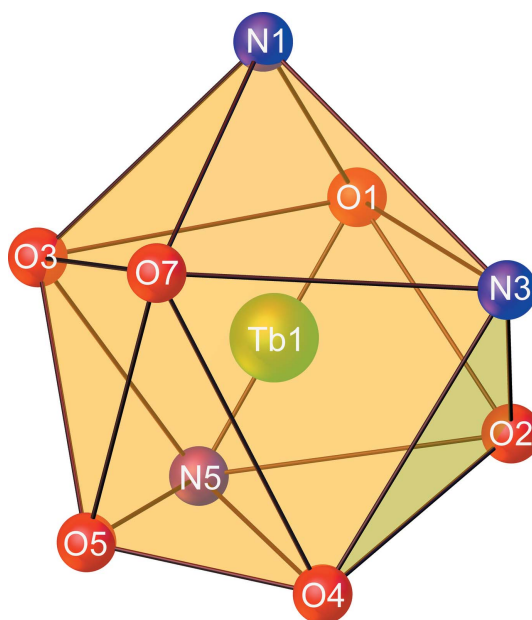


Figure 2
View of the distorted tricapped trigonal-prismatic coordination geometry of the central Tb^{3+} atom in **1**.

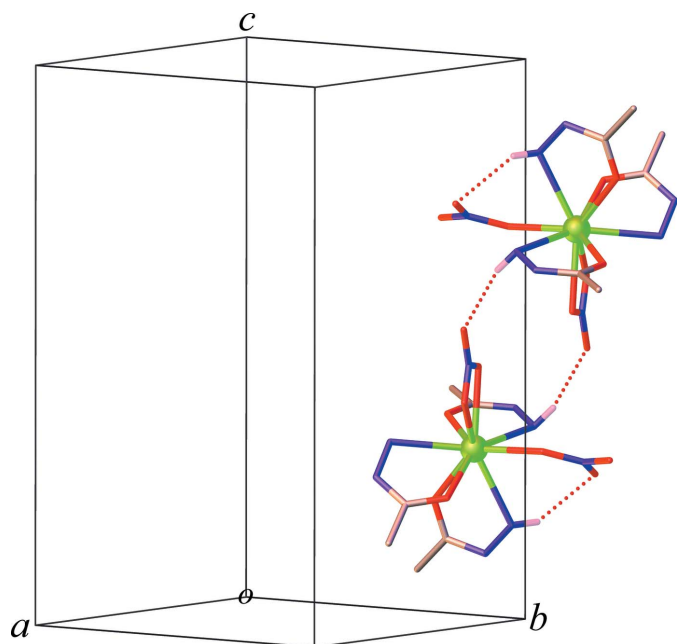


Figure 3
Dimer formation through N–H···O hydrogen bonds (dashed lines) in **1** (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

H3B···O6 hydrogen bonds involving the amine NH group of the acetohydrazide ligand and the coordinated nitrate oxygen atom, Fig. 3. Notably, the amine NH donor and the coordinated nitrate oxygen acceptor is also involved in an intramolecular N1–H1A···O8 hydrogen bond. The dimers are further held together through an intermolecular N3–H3A···O9 hydrogen bond between the amine NH and the coordinated nitrate oxygen (O9), resulting in the formation of a two-dimensional supramolecular layer that propagates in the [100] direction, Fig. 4. Ultimately, adjacent layers are connected into a three-dimensional supramolecular architecture *via* the other two complementary N–H···O hydrogen-bonding interactions (*i.e.* N5–H5B···O3 and N6–

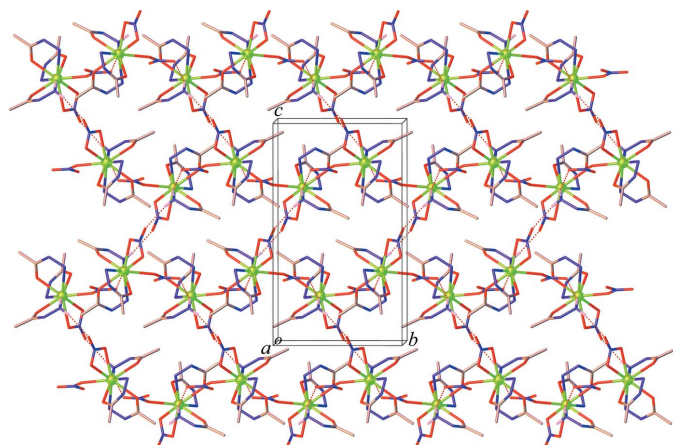


Figure 4
The two-dimensional hydrogen bonded layer in **1** (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

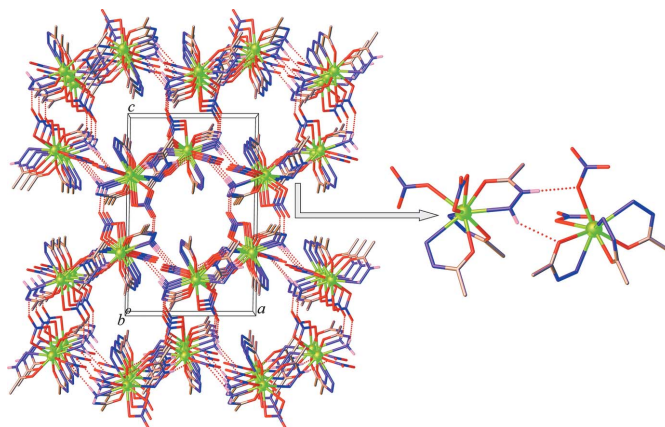


Figure 5
The three-dimensional hydrogen-bonded network in **1** (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

H6···O7) occurring between the acetohydrazide ligands and the coordinated nitrate ions, Fig. 5. In addition, the non-coordinated nitrate anion is located in cavities along the *b* axis and serves as the acceptor site for six N–H···O hydrogen-bonding interactions (*i.e.* N1–H1B···O10, N2–H2···O12, N4–H4···O10, N4–H4···O11, N5–H5A···O10, and N5–H5A···O12) as shown in Fig. 6.

4. Hirshfeld surface analysis

The Hirshfeld surface analysis (McKinnon *et al.*, 2007) and the associated two-dimensional fingerprint plot generation (Spackman & McKinnon, 2002) were carried out using *Crys-*

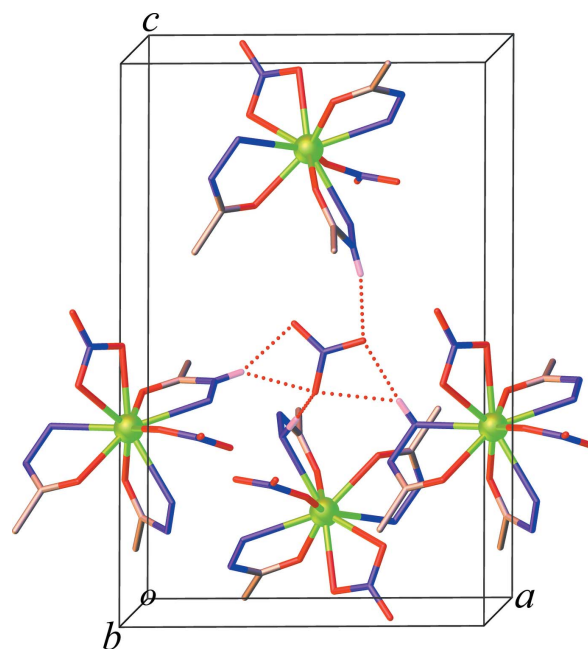


Figure 6
View of **1** approximately along the *b*-axis direction, showing the N–H···O hydrogen-bonding interactions involving the non-coordinated nitrate ion and the complex molecules (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

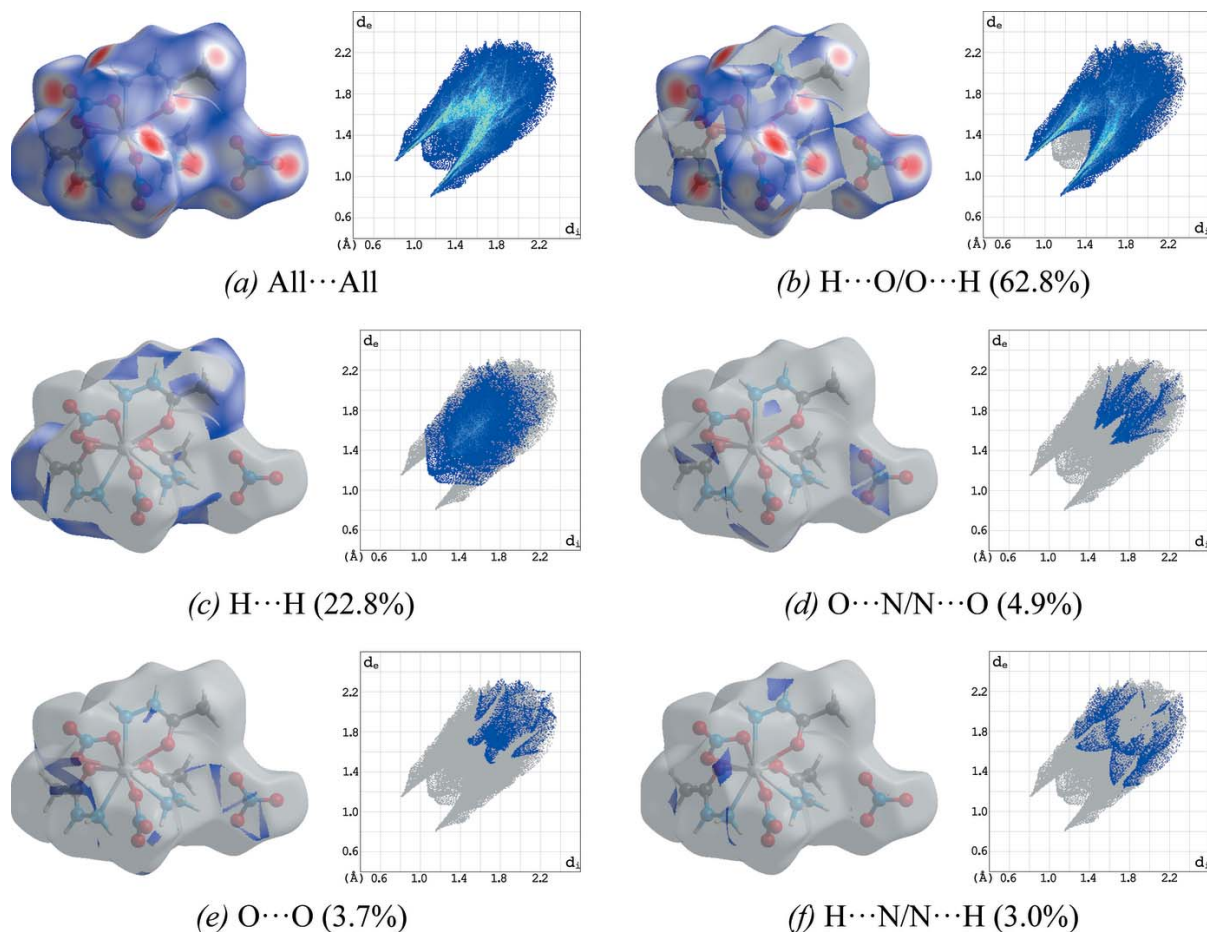


Figure 7

Two-dimensional fingerprint plots of **1**, showing (a) all interactions, and those delineated into (b) $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$, (c) $\text{H}\cdots\text{H}$, (d) $\text{N}\cdots\text{O}/\text{O}\cdots\text{N}$, (e) $\text{O}\cdots\text{O}$, and (f) $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$ contacts [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

talExplorer17 (Turner *et al.*, 2017) in order to quantify the nature of the intermolecular interactions present in the crystal structure, and the results are shown in Figs. 7 and 8. The most significant contributions to the d_{norm} surfaces are $\text{H}\cdots\text{O}/$

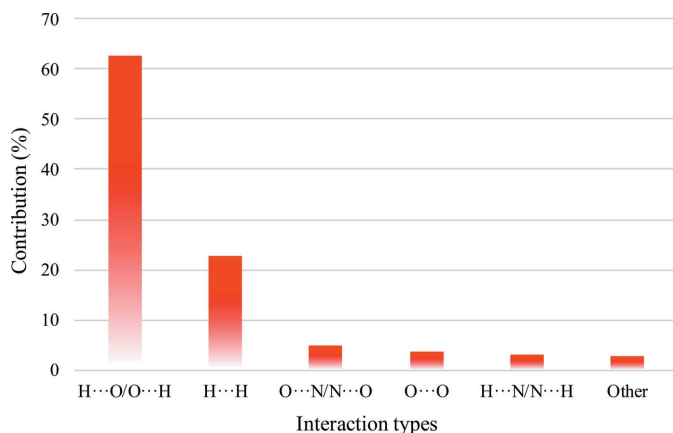


Figure 8

Quantitative results of different intermolecular contacts contributing to the Hirshfeld surface of **1**.

$\text{O}\cdots\text{H}$ contacts (*i.e.* $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds), contributing 62.8% to the overall crystal packing of the title compound. The $\text{H}\cdots\text{H}$ contacts (representing van der Waals interactions) with a 22.8% contribution play a minor role in the stabilization of the crystal packing. All other $\text{N}\cdots\text{O}/\text{O}\cdots\text{N}$, $\text{O}\cdots\text{O}$ and $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$ contacts make only negligible contributions to the Hirshfeld surface.

5. Database survey

A ConQuest search of the Cambridge Structural Database (CSD, Version 5.42, September 2021 update; Bruno *et al.*, 2002; Groom *et al.*, 2016) for the structures of lanthanide complexes with acetohydrazide ligands gave ten hits, *viz.* Er [CECLEB (Pangani *et al.*, 1983), CECLEB10 (Agre *et al.*, 1984)], Dy [CECLIF (Pangani *et al.*, 1983), CECLIF10 (Pangani, Agre *et al.*, 1984)], Ho [CECLOL (Pangani *et al.*, 1983), CECLOL10 (Pangani, Agre *et al.*, 1984)], Pr (CUWFAB; Pangani, Machhoshvili *et al.*, 1984), Gd (FOYGIM; Brandão *et al.*, 2020), and Sm [ISNHSM (Zinner *et al.*, 1979), QITBIH (Theppitak *et al.*, 2018)]. In all of these complexes, the acetohydrazide ligand adopts a $\mu_2-\kappa^1:\kappa^1$ bidentate chelating coordination mode to

bind the lanthanide(III) ion and the amine NH moiety of the acetohydrazide ligand can act as a donor site for intermolecular hydrogen-bonding interactions, similar to that of the title compound.

6. Synthesis and crystallization

A mixture of Tb(NO₃)₃·6H₂O (45.3 mg, 0.1 mmol), acetohydrazide (14.8 mg, 0.2 mmol), and isopropyl alcohol (4 ml) was sealed in a 15 ml Teflon-lined steel autoclave and heated at 373 K for 24 h. The mixture was cooled to room temperature and colorless block-shaped crystals of the title compound (**1**) were obtained in 87% yield (39.3 mg, based on Tb³⁺ source). Analysis calculated (%) for C₆H₁₈N₉O₁₂Tb: C 12.71; H 3.20; N 22.23%. Found: C 12.44; H 3.96; N 21.89%.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were located in difference-Fourier maps. All carbon-bound hydrogen atoms were placed in calculated positions and refined using a riding-model approximation with C–H = 0.96 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C). All nitrogen-bound hydrogen atoms were refined with a fixed distance N–H = 0.86 ± 0.02 Å.

Funding information

The authors gratefully acknowledge the financial support provided by the Thailand Institute of Nuclear Technology (Public Organization), through its program of TINT to University (grant to KC). This study was also partially supported by the Thammasat University Research Unit in Multifunctional Crystalline Materials and Applications (TU-McMa). CT would like to acknowledge a Graduate Development Scholarship 2020, National Research Council of Thailand (contract No. 15/2563).

References

Agre, V. M., Pangani, V. S. & Trunov, V. K. (1984). *Koord. Khim.* **10**, 120–128.
 Brandão, S. G., Ribeiro, M. A., Perrella, R. V., de Sousa Filho, P. C. & Luz, P. P. (2020). *J. Rare Earths*, **38**, 642–648.
 Bruker (2016). *APEX3*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
 Chen, P., Zhang, M., Sun, W., Li, H., Zhao, L. & Yan, P. (2015). *CrystEngComm*, **17**, 5066–5073.
 Cui, Y., Zhang, J., He, H. & Qian, G. (2018). *Chem. Soc. Rev.* **47**, 5740–5785.
 Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
 Janicki, R., Mondry, A. & Starynowicz, P. (2017). *Coord. Chem. Rev.* **340**, 98–133.
 Kuwamura, N. & Konno, T. (2021). *Inorg. Chem. Front.* **8**, 2634–649.

Table 2

Experimental details.

Crystal data	
Chemical formula	[Tb(NO ₃) ₂ (C ₂ H ₆ N ₂ O) ₃]NO ₃
<i>M_r</i>	567.21
Crystal system, space group	Monoclinic, <i>P</i> ₂ / <i>n</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.9076 (3), 9.7786 (3), 16.8578 (5)
β (°)	90.791 (1)
<i>V</i> (Å ³)	1797.90 (9)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.02
Crystal size (mm)	0.28 × 0.21 × 0.2
Data collection	
Diffractometer	Bruker D8 QUEST CMOS
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2016)
<i>T</i> _{min} , <i>T</i> _{max}	0.471, 0.747
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	47511, 6876, 5752
<i>R</i> _{int}	0.034
(sin θ/λ) _{max} (Å ⁻¹)	0.770
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.027, 0.044, 1.08
No. of reflections	6876
No. of parameters	293
No. of restraints	9
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.12, -1.13

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), and *OLEX2* (Dolomanov *et al.*, 2009).

Long, J., Lyubov, D. M., Mahrova, T. V., Cherkasov, A. V., Fukin, G. K., Guari, Y., Larionova, J. & Trifonov, A. A. (2018). *Dalton Trans.* **47**, 5153–5156.
 McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
 Pangani, V. S., Agre, V. M. & Trunov, V. K. (1983). *Zh. Neorg. Khim.* **28**, 2136–2137.
 Pangani, V. S., Agre, V. M., Trunov, V. K. & Machkhoshvili, R. I. (1984). *Koord. Khim.* **10**, 1128–1131.
 Pangani, V. S., Machkhoshvili, R. I., Agre, V. M., Trunov, V. K. & Shchelokov, R. N. (1984). *Inorg. Chim. Acta*, **94**, 79.
 Roy, S., Chakraborty, A. & Maji, T. P. (2014). *Coord. Chem. Rev.* **273–274**, 139–164.
 Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
 Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
 Spackman, M. A. & McKinnon, J. J. (2002). *CrystEngComm*, **4**, 378–392.
 Theppitak, C., Jiajaroen, S., Chongboriboon, N., Chanthee, S., Kielar, F., Dungkaew, W., Sukwattanasinitt, M. & Chainok, K. (2021b). *Molecules*, **26**, 4428.
 Theppitak, C., Kielar, F. & Chainok, K. (2018). *Acta Cryst.* **E74**, 1691–1694.
 Theppitak, C., Kielar, F., Dungkaew, W., Sukwattanasinitt, M., Kangkaew, L., Sahasithiwat, S., Zenno, H., Hayami, S. & Chainok, K. (2021a). *RSC Adv.* **11**, 24709–24721.
 Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. The University of Western Australia.
 Zinner, L. B., Crotty, D. E., Anderson, T. J. & Glick, M. D. (1979). *Inorg. Chem.* **18**, 2045–2048.

supporting information

Acta Cryst. (2022). E78, 354-358 [https://doi.org/10.1107/S2056989022002298]

Crystal structure and Hirshfeld surface analysis of tris(acetohydrazide- κ^2N,O)(nitrato- κO)(nittrato- κ^2O,O')terbium(III) nitrate

Chatphorn Theppitak, Sakchai Laksee and Kittipong Chainok

Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *ShelXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Tris(acetohydrazide- κ^2N,O)(nittrato- κO)(nittrato- κ^2O,O')terbium(III) nitrate]

Crystal data

[Tb(NO₃)₂(C₂H₆N₂O)₃]NO₃

$M_r = 567.21$

Monoclinic, $P2_1/n$

$a = 10.9076$ (3) Å

$b = 9.7786$ (3) Å

$c = 16.8578$ (5) Å

$\beta = 90.791$ (1)°

$V = 1797.90$ (9) Å³

$Z = 4$

$F(000) = 1112$

$D_x = 2.096$ Mg m⁻³

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

Cell parameters from 9937 reflections

$\theta = 3.0$ – 33.1 °

$\mu = 4.01$ mm⁻¹

$T = 296$ K

Block, colourless

$0.28 \times 0.21 \times 0.2$ mm

Data collection

Bruker D8 QUEST CMOS
diffractometer

Radiation source: sealed x-ray tube, Mo

Graphite monochromator

Detector resolution: 7.39 pixels mm⁻¹

ω and ϕ scans

Absorption correction: multi-scan
(SADABS; Bruker, 2016)

$T_{\min} = 0.471$, $T_{\max} = 0.747$

47511 measured reflections

6876 independent reflections

5752 reflections with $I > 2\sigma(I)$

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

$\theta_{\max} = 33.2$ °, $\theta_{\min} = 2.8$ °

$h = -16 \rightarrow 14$

$k = -15 \rightarrow 14$

$l = -25 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.044$

$S = 1.08$

6876 reflections

293 parameters

9 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0127P)^2 + 1.6017P]$

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

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 1.12$ e Å⁻³

$\Delta\rho_{\min} = -1.13$ e Å⁻³

Extinction correction: SHELXL2018/3
 (Sheldrick, 2015b),
 $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00248 (11)

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.

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	0.53793 (2)	0.69267 (2)	0.81234 (2)	0.01794 (3)
O1	0.53302 (15)	0.88900 (15)	0.73061 (9)	0.0316 (3)
O2	0.48569 (13)	0.88947 (16)	0.88653 (10)	0.0310 (3)
O3	0.68110 (13)	0.63211 (16)	0.71532 (9)	0.0275 (3)
O4	0.5610 (2)	0.6421 (2)	0.95580 (11)	0.0535 (5)
O5	0.68865 (16)	0.53978 (19)	0.88111 (12)	0.0425 (4)
O6	0.7062 (2)	0.5199 (3)	1.00927 (15)	0.0780 (8)
O7	0.47104 (13)	0.45766 (15)	0.79809 (10)	0.0297 (3)
O8	0.27693 (15)	0.46317 (18)	0.76534 (12)	0.0430 (4)
O9	0.37120 (17)	0.26983 (17)	0.77663 (12)	0.0431 (4)
O10	0.51235 (17)	0.6218 (2)	0.38477 (11)	0.0446 (4)
O11	0.57284 (17)	0.6504 (3)	0.50502 (13)	0.0598 (6)
O12	0.38755 (14)	0.70400 (18)	0.47151 (9)	0.0337 (4)
N1	0.4200 (2)	0.6697 (2)	0.67879 (12)	0.0302 (4)
H1A	0.3464 (17)	0.647 (3)	0.6859 (16)	0.040 (8)*
H1B	0.454 (3)	0.608 (3)	0.6519 (16)	0.050 (9)*
N2	0.42249 (18)	0.7916 (2)	0.63406 (11)	0.0294 (4)
H2	0.401 (3)	0.789 (3)	0.5854 (11)	0.048 (9)*
N3	0.31650 (17)	0.7017 (2)	0.86115 (13)	0.0301 (4)
H3A	0.265 (2)	0.694 (3)	0.8222 (13)	0.038 (7)*
H3B	0.302 (3)	0.635 (2)	0.8919 (16)	0.051 (9)*
N4	0.29181 (17)	0.8249 (2)	0.90180 (12)	0.0327 (4)
H4	0.2186 (19)	0.842 (3)	0.9187 (18)	0.060 (10)*
N5	0.74028 (16)	0.82302 (19)	0.82323 (11)	0.0243 (4)
H5A	0.786 (2)	0.809 (3)	0.8643 (13)	0.040 (8)*
H5B	0.722 (2)	0.9075 (18)	0.8197 (16)	0.040 (8)*
N6	0.81190 (16)	0.79567 (19)	0.75554 (12)	0.0274 (4)
H6	0.8761 (18)	0.842 (2)	0.7489 (15)	0.035 (7)*
N7	0.6533 (2)	0.5651 (2)	0.95054 (14)	0.0433 (5)
N8	0.36977 (17)	0.39549 (19)	0.77997 (11)	0.0290 (4)
N9	0.49126 (17)	0.6579 (2)	0.45403 (11)	0.0286 (4)
C1	0.48401 (19)	0.8957 (2)	0.66389 (13)	0.0258 (4)
C2	0.4922 (3)	1.0227 (3)	0.61533 (16)	0.0426 (6)
H2A	0.472625	1.100447	0.647550	0.064*
H2B	0.435281	1.017233	0.571491	0.064*

H2C	0.573927	1.032232	0.595665	0.064*
C3	0.38049 (19)	0.9150 (2)	0.90919 (12)	0.0246 (4)
C4	0.3478 (2)	1.0492 (3)	0.94566 (15)	0.0376 (5)
H4A	0.401145	1.066733	0.990255	0.056*
H4B	0.264351	1.046395	0.963032	0.056*
H4C	0.356757	1.120640	0.907122	0.056*
C5	0.77501 (18)	0.7031 (2)	0.70400 (13)	0.0246 (4)
C6	0.8488 (2)	0.6862 (3)	0.63059 (16)	0.0421 (6)
H6A	0.895336	0.603072	0.634062	0.063*
H6B	0.903604	0.762411	0.625384	0.063*
H6C	0.794817	0.682378	0.585182	0.063*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tb1	0.01473 (4)	0.01950 (5)	0.01956 (5)	0.00037 (4)	-0.00101 (3)	-0.00128 (4)
O1	0.0418 (9)	0.0248 (8)	0.0279 (8)	-0.0019 (7)	-0.0130 (7)	0.0027 (6)
O2	0.0230 (7)	0.0316 (8)	0.0386 (9)	-0.0015 (6)	0.0073 (6)	-0.0121 (7)
O3	0.0225 (7)	0.0280 (8)	0.0321 (8)	-0.0051 (6)	0.0061 (6)	-0.0090 (6)
O4	0.0599 (13)	0.0684 (13)	0.0320 (10)	0.0158 (11)	-0.0029 (9)	0.0067 (9)
O5	0.0319 (9)	0.0424 (10)	0.0530 (12)	0.0057 (8)	-0.0068 (8)	0.0097 (9)
O6	0.0641 (14)	0.102 (2)	0.0668 (15)	-0.0119 (14)	-0.0300 (12)	0.0547 (14)
O7	0.0236 (7)	0.0240 (7)	0.0414 (9)	-0.0037 (6)	-0.0017 (6)	-0.0023 (7)
O8	0.0224 (8)	0.0387 (10)	0.0679 (13)	0.0003 (7)	-0.0027 (8)	0.0016 (9)
O9	0.0467 (11)	0.0227 (8)	0.0598 (12)	-0.0082 (8)	-0.0065 (9)	0.0001 (8)
O10	0.0487 (11)	0.0525 (11)	0.0331 (9)	0.0088 (9)	0.0142 (8)	-0.0051 (8)
O11	0.0280 (9)	0.1001 (17)	0.0510 (12)	0.0141 (10)	-0.0115 (9)	-0.0132 (12)
O12	0.0214 (7)	0.0512 (10)	0.0284 (8)	0.0049 (7)	0.0009 (6)	-0.0029 (7)
N1	0.0331 (10)	0.0294 (10)	0.0278 (9)	-0.0056 (8)	-0.0048 (8)	-0.0015 (8)
N2	0.0332 (10)	0.0370 (11)	0.0178 (8)	-0.0010 (8)	-0.0041 (7)	0.0008 (8)
N3	0.0217 (8)	0.0310 (10)	0.0377 (11)	-0.0035 (8)	0.0021 (8)	-0.0029 (9)
N4	0.0198 (8)	0.0376 (11)	0.0410 (11)	0.0027 (8)	0.0094 (8)	-0.0069 (9)
N5	0.0234 (8)	0.0233 (9)	0.0261 (9)	-0.0011 (7)	-0.0032 (7)	-0.0024 (7)
N6	0.0213 (8)	0.0257 (9)	0.0352 (10)	-0.0075 (7)	0.0036 (7)	-0.0022 (8)
N7	0.0389 (11)	0.0437 (13)	0.0470 (13)	-0.0100 (10)	-0.0171 (10)	0.0220 (11)
N8	0.0277 (9)	0.0257 (9)	0.0337 (10)	-0.0065 (8)	0.0027 (8)	-0.0008 (8)
N9	0.0237 (9)	0.0321 (10)	0.0300 (9)	-0.0011 (7)	0.0041 (7)	0.0022 (8)
C1	0.0233 (10)	0.0299 (11)	0.0242 (9)	0.0054 (8)	0.0013 (8)	0.0019 (8)
C2	0.0429 (14)	0.0443 (14)	0.0404 (14)	-0.0028 (12)	-0.0072 (11)	0.0157 (12)
C3	0.0248 (9)	0.0301 (10)	0.0189 (9)	0.0048 (9)	0.0016 (7)	-0.0013 (8)
C4	0.0361 (12)	0.0364 (13)	0.0403 (13)	0.0112 (10)	0.0027 (10)	-0.0104 (11)
C5	0.0221 (9)	0.0221 (9)	0.0296 (10)	0.0016 (8)	0.0035 (8)	0.0010 (8)
C6	0.0414 (13)	0.0411 (14)	0.0445 (14)	-0.0059 (12)	0.0206 (11)	-0.0097 (12)

Geometric parameters (Å, °)

Tb1—O1	2.3632 (15)	N2—H2	0.849 (17)
Tb1—O2	2.3690 (15)	N2—C1	1.316 (3)

Tb1—O3	2.3525 (14)	N3—H3A	0.865 (17)
Tb1—O4	2.4779 (19)	N3—H3B	0.850 (17)
Tb1—O5	2.4959 (17)	N3—N4	1.414 (3)
Tb1—O7	2.4220 (15)	N4—H4	0.867 (17)
Tb1—N1	2.587 (2)	N4—C3	1.313 (3)
Tb1—N3	2.5640 (19)	N5—H5A	0.857 (17)
Tb1—N5	2.5532 (18)	N5—H5B	0.851 (17)
O1—C1	1.240 (2)	N5—N6	1.417 (3)
O2—C3	1.240 (2)	N6—H6	0.845 (17)
O3—C5	1.254 (2)	N6—C5	1.314 (3)
O4—N7	1.261 (3)	C1—C2	1.491 (3)
O5—N7	1.262 (3)	C2—H2A	0.9600
O6—N7	1.222 (3)	C2—H2B	0.9600
O7—N8	1.294 (2)	C2—H2C	0.9600
O8—N8	1.232 (2)	C3—C4	1.494 (3)
O9—N8	1.230 (2)	C4—H4A	0.9600
O10—N9	1.244 (2)	C4—H4B	0.9600
O11—N9	1.231 (3)	C4—H4C	0.9600
O12—N9	1.257 (2)	C5—C6	1.494 (3)
N1—H1A	0.844 (17)	C6—H6A	0.9600
N1—H1B	0.845 (17)	C6—H6B	0.9600
N1—N2	1.411 (3)	C6—H6C	0.9600
O1—Tb1—O2	69.15 (6)	H3A—N3—H3B	106 (3)
O1—Tb1—O4	137.09 (7)	N4—N3—Tb1	111.81 (13)
O1—Tb1—O5	140.08 (6)	N4—N3—H3A	108.2 (18)
O1—Tb1—O7	135.12 (5)	N4—N3—H3B	109 (2)
O1—Tb1—N1	63.66 (6)	N3—N4—H4	120 (2)
O1—Tb1—N3	98.35 (6)	C3—N4—N3	118.22 (18)
O1—Tb1—N5	69.45 (6)	C3—N4—H4	121 (2)
O2—Tb1—O4	70.66 (7)	Tb1—N5—H5A	118.0 (19)
O2—Tb1—O5	113.77 (6)	Tb1—N5—H5B	106.4 (19)
O2—Tb1—O7	138.48 (5)	H5A—N5—H5B	110 (3)
O2—Tb1—N1	114.19 (6)	N6—N5—Tb1	109.48 (12)
O2—Tb1—N3	64.41 (6)	N6—N5—H5A	107.6 (19)
O2—Tb1—N5	76.73 (5)	N6—N5—H5B	104.8 (19)
O3—Tb1—O1	79.00 (6)	N5—N6—H6	118.1 (18)
O3—Tb1—O2	137.59 (5)	C5—N6—N5	119.68 (17)
O3—Tb1—O4	124.67 (6)	C5—N6—H6	122.1 (18)
O3—Tb1—O5	74.51 (6)	O4—N7—O5	115.89 (19)
O3—Tb1—O7	83.93 (5)	O6—N7—O4	121.8 (3)
O3—Tb1—N1	72.54 (6)	O6—N7—O5	122.3 (3)
O3—Tb1—N3	150.36 (6)	O8—N8—O7	119.45 (18)
O3—Tb1—N5	66.06 (5)	O9—N8—O7	117.96 (19)
O4—Tb1—O5	50.93 (7)	O9—N8—O8	122.57 (19)
O4—Tb1—N1	150.97 (7)	O10—N9—O12	120.03 (19)
O4—Tb1—N3	77.11 (7)	O11—N9—O10	119.8 (2)
O4—Tb1—N5	87.34 (7)	O11—N9—O12	120.1 (2)

O5—Tb1—N1	131.95 (7)	O1—C1—N2	121.1 (2)
O5—Tb1—N3	119.27 (7)	O1—C1—C2	120.9 (2)
O5—Tb1—N5	72.69 (6)	N2—C1—C2	118.0 (2)
O7—Tb1—O4	86.19 (7)	C1—C2—H2A	109.5
O7—Tb1—O5	70.93 (6)	C1—C2—H2B	109.5
O7—Tb1—N1	71.68 (6)	C1—C2—H2C	109.5
O7—Tb1—N3	77.33 (6)	H2A—C2—H2B	109.5
O7—Tb1—N5	137.71 (5)	H2A—C2—H2C	109.5
N3—Tb1—N1	79.81 (7)	H2B—C2—H2C	109.5
N5—Tb1—N1	121.66 (6)	O2—C3—N4	121.3 (2)
N5—Tb1—N3	140.98 (6)	O2—C3—C4	122.1 (2)
C1—O1—Tb1	125.30 (14)	N4—C3—C4	116.64 (19)
C3—O2—Tb1	123.84 (14)	C3—C4—H4A	109.5
C5—O3—Tb1	121.19 (13)	C3—C4—H4B	109.5
N7—O4—Tb1	96.95 (15)	C3—C4—H4C	109.5
N7—O5—Tb1	96.06 (14)	H4A—C4—H4B	109.5
N8—O7—Tb1	136.41 (13)	H4A—C4—H4C	109.5
Tb1—N1—H1A	111.2 (19)	H4B—C4—H4C	109.5
Tb1—N1—H1B	108 (2)	O3—C5—N6	121.60 (19)
H1A—N1—H1B	108 (3)	O3—C5—C6	121.0 (2)
N2—N1—Tb1	112.25 (13)	N6—C5—C6	117.39 (19)
N2—N1—H1A	109.1 (19)	C5—C6—H6A	109.5
N2—N1—H1B	108 (2)	C5—C6—H6B	109.5
N1—N2—H2	119 (2)	C5—C6—H6C	109.5
C1—N2—N1	117.60 (18)	H6A—C6—H6B	109.5
C1—N2—H2	122 (2)	H6A—C6—H6C	109.5
Tb1—N3—H3A	111.3 (19)	H6B—C6—H6C	109.5
Tb1—N3—H3B	110 (2)		
Tb1—O1—C1—N2	3.9 (3)	Tb1—O7—N8—O9	178.18 (15)
Tb1—O1—C1—C2	-176.58 (17)	Tb1—N1—N2—C1	1.4 (2)
Tb1—O2—C3—N4	8.5 (3)	Tb1—N3—N4—C3	0.0 (3)
Tb1—O2—C3—C4	-171.10 (16)	Tb1—N5—N6—C5	-6.9 (2)
Tb1—O3—C5—N6	14.8 (3)	N1—N2—C1—O1	-3.4 (3)
Tb1—O3—C5—C6	-164.56 (17)	N1—N2—C1—C2	177.1 (2)
Tb1—O4—N7—O5	-4.1 (2)	N3—N4—C3—O2	-5.3 (3)
Tb1—O4—N7—O6	174.7 (2)	N3—N4—C3—C4	174.4 (2)
Tb1—O5—N7—O4	4.0 (2)	N5—N6—C5—O3	-4.1 (3)
Tb1—O5—N7—O6	-174.7 (2)	N5—N6—C5—C6	175.3 (2)
Tb1—O7—N8—O8	-0.5 (3)		

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>
N1—H1A...O8	0.84 (2)	2.37 (2)	2.950 (3)	126 (2)
N1—H1B...O10 ⁱ	0.85 (2)	2.36 (2)	3.136 (3)	153 (3)
N2—H2...O11	0.85 (2)	2.69 (3)	3.070 (3)	109 (2)
N2—H2...O12	0.85 (2)	2.09 (2)	2.891 (2)	156 (3)

N3—H3A···O8	0.87 (2)	2.46 (3)	2.866 (3)	110 (2)
N3—H3A···O9 ⁱⁱ	0.87 (2)	2.33 (2)	3.146 (3)	157 (2)
N3—H3B···O6 ⁱⁱⁱ	0.85 (2)	2.25 (2)	3.089 (3)	168 (3)
N4—H4···O10 ^{iv}	0.87 (2)	2.34 (2)	3.102 (3)	147 (3)
N4—H4···O11 ^{iv}	0.87 (2)	2.17 (2)	2.984 (3)	156 (3)
N5—H5A···O10 ^v	0.86 (2)	2.58 (2)	3.176 (3)	128 (2)
N5—H5A···O12 ^v	0.86 (2)	2.11 (2)	2.964 (2)	173 (3)
N5—H5B···O3 ^{vi}	0.85 (2)	2.51 (2)	3.211 (2)	140 (2)
N6—H6···O7 ^{vi}	0.85 (2)	2.17 (2)	2.999 (2)	166 (2)
N6—H6···O10 ^v	0.85 (2)	2.74 (2)	3.170 (3)	114 (2)

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