Crystal structure and Hirshfeld surface analysis of tris(acetohydrazide-$\kappa^2N,O$)(nitrato-$\kappa^2O$)(nitrato-$\kappa^2O,O'$)terbium(III) nitrate

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In the title lanthanide(III) compound, [Tb(NO$_3$)$_2$(C$_2$H$_6$N$_2$O)$_3$]NO$_3$, the asymmetric unit contains one Tb$^{3+}$ ion, three acetohydrazide (C$_2$H$_6$N$_2$O) 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···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$^{3+}$ ion with good recyclability (Theppitak et al., 2021b).

In this work, we present the molecular structure of a new terbium(III) complex, [Tb(C$_2$H$_6$N$_2$O)$_3$(NO$_3$)$_3$]NO$_3$ (I), synthesized with acetohydrazide (C$_2$H$_6$N$_2$O) 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 Tb³⁺ ion, three acetohydrazide ligands, two coordinated nitrate anions, and a non-coordinated nitrate counter-anion. The Tb³⁺ ion is ninefold coordinated (TbN₃O₆) 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 Tb³⁺ 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 Tb—O bond lengths of 2.353 (2)–2.496 (2) Å are slightly shorter than the Tb—N bond lengths [2.553 (2)–2.586 (2) Å]. The bond angles around the central Tb³⁺ ion fall into the range of 50.93 (7)–150.97 (7)°. These values are comparable to those reported for other ninefold-coordinated Tb³⁺ compounds containing oxygen/nitrogen-donor ligands such as [Tb(C₁₇H₁₃N₃)(NO₃)₂·(DMSO)]·CH₃OH (VUKNEW, Chen et al., 2015) and [Tb(C₁₃H₂₂N₃)(NO₃)₃]·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 [Tb(C₂H₆N₂O)₃(NO₃)₃]⁺ complex molecules form centrosymmetric dimers via pairs of symmetry-related N₃–

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### Table 1

| D—H···A | D—H (Å) | H···A (Å) | D···A (Å) | D—H···A (°) |
|---------|---------|----------|----------|------------|
| N1—H1A—O8 | 0.84 (2) | 2.37 (2) | 2.950 (3) | 126 (2) |
| N1—H1B—O10⁰ | 0.85 (2) | 2.36 (2) | 3.136 (3) | 153 (2) |
| 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—O9⁰ | 0.87 (2) | 2.33 (2) | 3.146 (3) | 157 (2) |
| N3—H3B—O6² | 0.85 (2) | 2.25 (2) | 3.089 (3) | 168 (3) |
| N4—H4—O10⁰ | 0.87 (2) | 2.34 (2) | 3.102 (3) | 143 (3) |
| N4—H4—O11² | 0.87 (2) | 2.17 (2) | 2.984 (3) | 156 (3) |
| N5—H5A—O10⁰ | 0.86 (2) | 2.58 (2) | 3.176 (3) | 128 (2) |
| N5—H5A—O12² | 0.86 (2) | 2.11 (2) | 2.964 (2) | 173 (3) |
| N5—H5B—O3³ | 0.85 (2) | 2.51 (2) | 3.211 (2) | 140 (2) |
| N6—H6—O7⁷ | 0.85 (2) | 2.17 (2) | 2.999 (2) | 166 (2) |

Symmetry codes: (i) x+1, y+1, z+1; (ii) x, y+1, z+1; (iii) x+1, y, z+1; (iv) x, y, z+1; (v) x+1, y, z+1; (vi) x+1, y+1, z+1.
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—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-
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 $H \cdot \cdot \cdot O$ and $H \cdot \cdot \cdot H$ contacts (i.e. $N-H \cdot \cdot \cdot O$ hydrogen bonds), contributing 62.8% to the overall crystal packing of the title compound. The $H \cdot \cdot \cdot H$ contacts (representing van der Waals interactions) with a 22.8% contribution play a minor role in the stabilization of the crystal packing. All other $N \cdot \cdot \cdot O \cdot \cdot \cdot N$, $O \cdot \cdot \cdot O$ and $H \cdot \cdot \cdot N \cdot \cdot \cdot H$ 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), CECELIE10 (Agre et al., 1984)], Dy [CECLIF (Pangani et al., 1983), CECLIE10 (Pangani, Agre et al., 1984)], Ho [CECLOL (Pangani et al., 1983), CECELIE10 (Pangani, Agre et al., 1984)], Pr (CUWFAB; Pangani, Mach-hoshvili et al., 1984), Gd (FOYGIM; Branda˜o et al., 2020), and Sm [ISNHSM (Zinner et al., 1979), QITBIIH (Theppitak et al., 2018)]. In all of these complexes, the acetohydrazide ligand adopts a $\mu_2$-$k^1$ 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(NO$_3$)$_3$·6H$_2$O (45.3 mg, 0.1 mmol), acetohydrazide (14.8 mg, 0.02 mmol), and isopropyl alcohol (4 ml) was sealed in a 15 ml Teilon-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 Tb$^{3+}$ source). Analysis calculated (%) for C$_{26}$H$_{18}$N$_8$O$_{12}$Tb·C$_2$H$_6$N$_2$O·Tb: 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 $U_{iso}(H) = 1.5U_{eq}(C)$. All nitrogen-bound hydrogen atoms were refined with a fixed distance N—H = 0.86 ± 0.02 Å.

Funding information

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Table 2

| Experimental details. |
|-----------------------|
| **Crystal data**      |
| Chemical formula      | [Tb(NO$_3$)$_3$(C$_2$H$_6$N$_2$O)$_3$]NO$_3$ |
| $M_r$                 | 567.21                                      |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K)       | 296                                         |
| a, b, c (Å)           | 10.9076 (3), 9.7786 (3), 16.8578 (5)        |
| $\beta$ (°)          | 90.791 (1)                                  |
| $\mu$ (mm$^{-1}$)    | 1797.90 (9)                                 |
| Radiation type        | Mo Kα                                      |
| Crystal size (mm)     | 4.02                                        |
| Crystal size (mm)     | 0.28 $\times$ 0.21 $\times$ 0.2             |
| **Data collection**   |
| Diffractometer        | Bruker D8 QUEST CMOS                       |
| Absorption correction | Multi-scan (SADABS; Bruker, 2016)           |
| $\mathbf{\mathbf{I}}$ | 0.471, 0.747                                |
| No. of parameters     | 293                                         |
| No. of reflections    | 47511, 6876, 5752                           |
| $R_{int}$             | 0.034                                       |
| $\beta_{\max}$ (Å$^{-1}$) | 0.770                                    |
| Refinement            |
| $R[F^2 > 2\sigma(F^2)]$, wR(F$^2$), S | 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 |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å$^{-3}$) | 1.12, −1.13 |

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Crystal structure and Hirshfeld surface analysis of tris(acetohydrazide-κ²N,O) (nitrato-κO)(nitrato-κ²O,O')terbium(III) nitrate

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Computing details

Data collection: APEX3 (Bruker, 2016); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (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-κ²N,O)(nitrato-κO)(nitrato-κ²O,O')terbium(III) nitrate

Crystal data

[Tb(NO₃)₂(C₂H₆N₂O)₃]NO₃

- M_r = 567.21
- Monoclinic, P₂₁/n
- a = 10.9076 (3) Å
- b = 9.7786 (3) Å
- c = 16.8578 (5) Å
- β = 90.791 (1)°
- V = 1797.90 (9) Å³
- Z = 4

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)

| Tmin | Tmax |
|------|------|
| 0.471 | 0.747 |

Refinement

Refinement on F²
- Least-squares matrix: full
- R[F² > 2σ(F²)] = 0.027
- wR(F²) = 0.044
- S = 1.08
- 6876 reflections
- 293 parameters
- 9 restraints
- H atoms treated by a mixture of independent and constrained refinement

| Δρmax | Δρmin |
|-------|-------|
| 1.12 e Å⁻³ | -1.13 e Å⁻³ |

Acta Cryst. (2022). E78, 354-358 [https://doi.org/10.1107/S2056989022002298]
Extinction correction: SHELXL2018/3
(Sheldrick, 2015b),
Fc^2 = kFc[1+0.001xFc^2/sin(2θ)]^{-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 (Å²)

|    | x     | y     | z     | U(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*      |
| 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, °)**

| Bond          | Distance (Å) | Angle (°) |
|---------------|--------------|-----------|
| Tb1—O1        | 2.3632 (15)  |           |
| Tb1—O2        | 2.3690 (15)  |           |

*Supporting information*

*Acta Cryst. (2022).* E78, 354-358
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| 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) N4—C3—H4A 109.5
N8—O7—Tb1 136.41 (13) N4—C3—H4B 109.5
Tb1—N1—H1A 111.2 (19) N4—C3—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
N2—N1—Tb1 117.60 (18) C1—N2—N1 117.60 (18)
C1—N2—H2 122 (2) N2—N1—Tb1 117.60 (18)
Tb1—N3—H3A 111.3 (19) C1—N2—H2 122 (2)
Tb1—N3—H3B 110 (2)

\[
\begin{array}{cccc}
\text{D—H···A} & \text{D—H} & \text{H···A} & \text{D···A} & \text{D—H···A} \\
\hline
\text{N1—H1.4···O8} & 0.84 (2) & 2.37 (2) & 2.950 (3) & 126 (2) \\
\text{N1—H1B···O10'} & 0.85 (2) & 2.36 (2) & 3.136 (3) & 153 (3) \\
\text{N2—H2···O11} & 0.85 (2) & 2.69 (3) & 3.070 (3) & 109 (2) \\
\text{N2—H2···O12} & 0.85 (2) & 2.09 (2) & 2.891 (2) & 156 (3) \\
\end{array}
\]

Hydrogen-bond geometry (Å, °)

\[
\begin{array}{cccc}
\text{D—H···A} & \text{D—H} & \text{H···A} & \text{D···A} & \text{D—H···A} \\
\hline
\text{N1—H1.4···O8} & 0.84 (2) & 2.37 (2) & 2.950 (3) & 126 (2) \\
\text{N1—H1B···O10'} & 0.85 (2) & 2.36 (2) & 3.136 (3) & 153 (3) \\
\text{N2—H2···O11} & 0.85 (2) & 2.69 (3) & 3.070 (3) & 109 (2) \\
\text{N2—H2···O12} & 0.85 (2) & 2.09 (2) & 2.891 (2) & 156 (3) \\
\end{array}
\]
| Bond          | D (Å)  | d (Å)  | r (Å)  | Angle (°) |
|--------------|--------|--------|--------|-----------|
| N3–H3···O8   | 0.87 (2) | 2.46 (3) | 2.866 (3) | 110 (2)  |
| N3–H3···O9\textsuperscript{ii} | 0.87 (2) | 2.33 (2) | 3.146 (3) | 157 (2)  |
| N3–H3B···O6\textsuperscript{iii} | 0.85 (2) | 2.25 (2) | 3.089 (3) | 168 (3)  |
| N4–H4···O10\textsuperscript{iv} | 0.87 (2) | 2.34 (2) | 3.102 (3) | 147 (3)  |
| N4–H4···O11\textsuperscript{iv} | 0.87 (2) | 2.17 (2) | 2.984 (3) | 156 (3)  |
| N5–H5A···O10\textsuperscript{v} | 0.86 (2) | 2.58 (2) | 3.176 (3) | 128 (2)  |
| N5–H5A···O12\textsuperscript{v} | 0.86 (2) | 2.11 (2) | 2.964 (2) | 173 (3)  |
| N5–H5B···O3\textsuperscript{vi} | 0.85 (2) | 2.51 (2) | 3.211 (2) | 140 (2)  |
| N6–H6···O7\textsuperscript{vi} | 0.85 (2) | 2.17 (2) | 2.999 (2) | 166 (2)  |
| N6–H6···O10\textsuperscript{vi} | 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.