



Synthesis, crystal structure, Hirshfeld surface and void analysis of bis(μ_2 -4-aminobenzoato- κ^2 O:O')-bis[bis(4-aminobenzoato- κ^2 O,O')diaqua-thulium(III)] dihydrate

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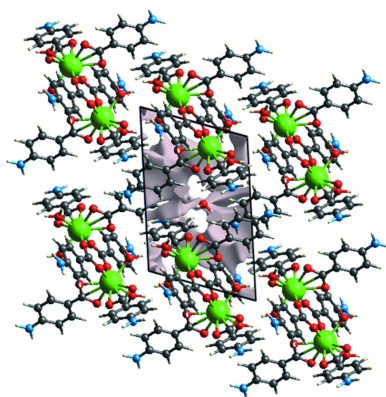
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The asymmetric unit of the title compound, [Tm₂(C₇H₆NO₂)₆(H₂O)₄]·2H₂O, contains three 4-aminobenzoate (**4ABA**) ligands, two coordinated water molecules, a thulium metal ion, and a water molecule of crystallization. The overall structure of the complex (**4ABA-Tm**) is in the form of a dimer. In the dinuclear thulium complex, symmetry-relevant TmO₈ coordination polyhedra are formed by the O atoms of two chelating 4-aminobenzoate ligands, the O atoms of two non-chelating 4-aminobenzoate ligands, and two water molecules. The Tm—O bond lengths range from 2.216 (3) to 2.471 (3) Å with the Tm···Tm separation in the dinuclear complex being 4.7863 (5) Å. The crystal structure features O—H···N, N—H···O, and O—H···O hydrogen-bonding interactions. Further stabilization of the crystal packing is due to C—H··· π and off-set π – π stacking interactions. Hirshfeld surface analysis indicates that H···H contacts are the most significant contributors to the crystal packing (45.9%). In addition, a void analysis was performed to check the strength of the crystal packing.

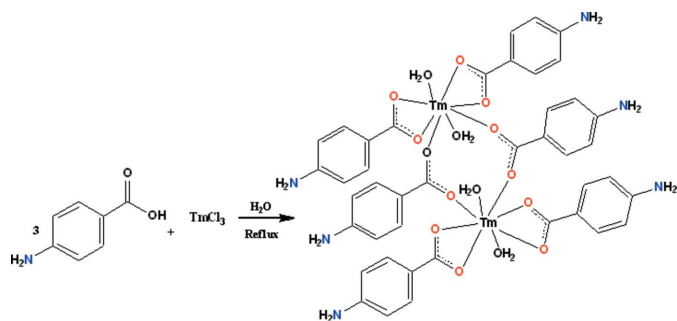
1. Chemical context

The coordination chemistry of rare-earth metals has been widely studied, and the structures of a significant variety of complexes with diverse kinds of ligands have been reported (You *et al.*, 2021). In particular, the lanthanide contraction along the series is of interest, and in a detailed analysis of this phenomenon using elements from the lanthanide series, *p*-aminobenzoic acid (HL) was found to be a very useful and biologically important ligand (Smith & Lynch, 2015). The carboxylate group of HL can be coordinated with the metals simultaneously in three different modes, namely chelating, bridging, and chelating-bridging (Ali *et al.*, 2014). In the complexes of HL with alkali metals such as Na⁺ or K⁺, the ligand is not directly coordinated to the metal ion, but rather it is surrounded by coordinated water molecules (You *et al.*, 2021). Both the carboxylic and amino groups of the ligand are coordinated to the metal in complexes with Ba²⁺, Ag⁺, Zn²⁺, Cd²⁺, and Ni²⁺ (Mamedov *et al.*, 1982; Amiraslanov *et al.*, 1982*a*), while only the oxygen atoms of the carboxylic groups are coordinated to the metal ion in complexes of Sr²⁺, Mg²⁺, and Co²⁺ with this ligand (Amiraslanov *et al.*, 1982*b*; Sun *et al.*, 2004). In comparison to the above coordination diversity, in the complexes of HL with rare-earth elements like Nd⁺³ and



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Sm^{+3} (Khiyalov *et al.*, 1981; Mao & Lianq, 2016), only the nitrogen atom of the amino group is coordinated by the central metal atom, while in complexes of Lu^{+3} and Ho^{+3} with HL (Sun *et al.*, 2004), the nitrogen atom of the amino group is not coordinated while the ligands are attached to the metal atom by the oxygen atoms of the carboxylate moiety. In this context, we report the synthesis, crystal structure, Hirshfeld surface, void, thermogravimetric and FT-IR analysis of the title compound, $[\text{Tm}_2(\text{C}_7\text{H}_6\text{NO}_2)_6(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$, which is closely related to its Lu^{+3} and Ho^{+3} analogues (Sun *et al.*, 2004).



2. Structural commentary

The asymmetric unit of the title compound **4ABA-Tm** (Fig. 1) contains a centrosymmetric thulium dinuclear complex and one water molecule of crystallization. Each Tm^{III} atom is octacoordinated by two chelating 4-aminobenzoate ligands, two bridging 4-aminobenzoate ligands and two coordinated water molecules. In the coordination sphere, bond lengths range from 2.216 (3) to 2.471 (3) Å, while bond angles range from 53.82 (10) to 161.28 (12)° (Table 1). The $\text{Tm}\cdots\text{Tm}^{\text{i}}$ separation in the **4ABA-Tm** complex is 4.7863 (5) Å (Table 1).

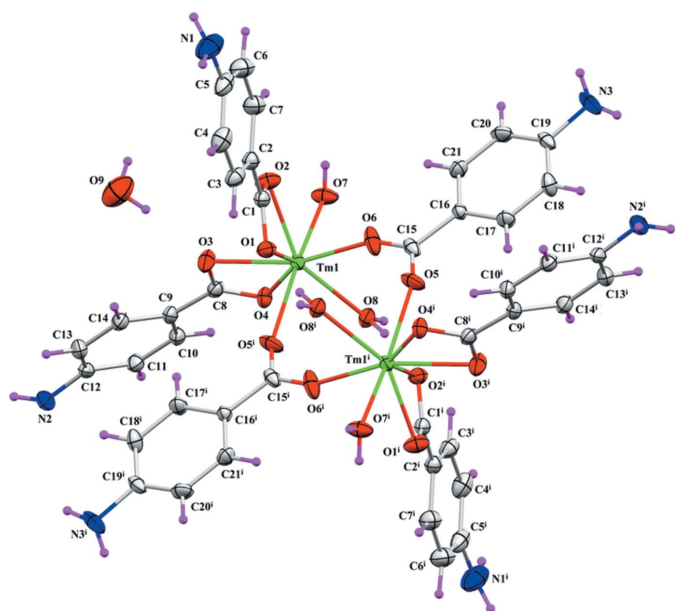


Figure 1
 ORTEP view of **4ABA-Tm** with ellipsoids drawn at a 30% probability level with H atoms shown as small circles of arbitrary radii.

Table 1
 Selected geometric parameters (Å, °).

Tm1—O5	2.216 (3)	Tm1—O3	2.374 (3)
Tm1—O6 ⁱ	2.223 (3)	Tm1—O8	2.382 (3)
Tm1—O7	2.293 (3)	Tm1—O4	2.457 (3)
Tm1—O2	2.329 (3)	Tm1—O1	2.471 (3)
O5—Tm1—O6 ⁱ	108.53 (13)	O3—Tm1—O8	124.48 (11)
O5—Tm1—O7	156.90 (13)	O5—Tm1—O4	80.34 (11)
O6 ⁱ —Tm1—O7	84.40 (13)	O6 ⁱ —Tm1—O4	142.65 (11)
O5—Tm1—O2	125.29 (12)	O7—Tm1—O4	78.06 (11)
O6 ⁱ —Tm1—O2	81.97 (13)	O2—Tm1—O4	123.35 (10)
O7—Tm1—O2	74.42 (11)	O3—Tm1—O4	53.82 (10)
O5—Tm1—O3	80.05 (12)	O8—Tm1—O4	72.41 (10)
O6 ⁱ —Tm1—O3	161.28 (12)	O5—Tm1—O1	75.80 (11)
O7—Tm1—O3	93.61 (13)	O6 ⁱ —Tm1—O1	76.29 (11)
O2—Tm1—O3	79.58 (11)	O7—Tm1—O1	126.75 (11)
O5—Tm1—O8	78.30 (11)	O2—Tm1—O1	54.20 (10)
O6 ⁱ —Tm1—O8	74.11 (12)	O3—Tm1—O1	90.29 (10)
O7—Tm1—O8	87.42 (11)	O8—Tm1—O1	131.47 (10)
O2—Tm1—O8	151.26 (11)	O4—Tm1—O1	139.92 (9)

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

The oxygen atoms O2 of the first 4-aminobenzoate chelate (ligand A, C1–C7/N1/O1/O2), O4 of the second 4-aminobenzoate chelate (ligand B, C8–C14/N2/O3/O4) and O5 of the 4-aminobenzoate non-chelate (ligand C, C15–C21/N3/O5/O6) show maximum deviations from their respective planes with values of 0.1748 (3) Å for O2, 0.3087 (3) Å for O4, and 0.1351 (3) Å for O5. Ligand B is twisted at a dihedral angle of 70.83 (7)° with respect to ligand A. The non-chelating ligand C is twisted at dihedral angles of 79.7 (9) and 72.7 (9)°, respectively, to the planes of ligands A and B. Intramolecular O—H \cdots O hydrogen bonding (Table 2) involving OH from the non-coordinating water and the O atom (hydrogen-bond acceptor) of the chelating 4-aminobenzoate ligand stabilizes the molecular configuration.

3. Supramolecular features

The centrosymmetric dinuclear thulium complexes are linked through O—H \cdots O, O—H \cdots N and N—H \cdots O hydrogen-bonding interactions. A C11 chain running along the *b*-axis

Table 2
 Hydrogen-bond geometry (Å, °).

Cg3 is the centroid of the C16–C21 ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O7—H7A \cdots N3 ⁱⁱ	0.82 (1)	1.95 (2)	2.753 (6)	169 (5)
O7—H7B \cdots N2 ⁱⁱⁱ	0.82 (1)	2.18 (2)	2.940 (5)	154 (5)
O8—H8A \cdots O1 ⁱ	0.82 (1)	1.98 (1)	2.791 (4)	172 (4)
O8—H8B \cdots O4 ^{iv}	0.82 (1)	1.96 (1)	2.780 (4)	174 (4)
N1—H1B \cdots O9 ^v	0.85 (1)	2.06 (3)	2.870 (8)	158 (7)
N2—H2B \cdots O9 ^{vi}	0.85 (1)	2.24 (2)	3.051 (7)	161 (5)
N3—H3B \cdots O5 ^{vii}	0.84 (1)	2.46 (3)	3.173 (6)	144 (5)
N3—H3B \cdots O8 ^{vii}	0.84 (1)	2.56 (5)	3.092 (5)	122 (4)
O9—H9A \cdots O3	0.83 (1)	2.00 (1)	2.828 (6)	172 (7)
O9—H9B \cdots O2 ^{viii}	0.84 (1)	2.34 (6)	2.849 (6)	119 (5)
C11—H11 \cdots Cg3 ^{ix}	0.93	2.68	3.538 (5)	155

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

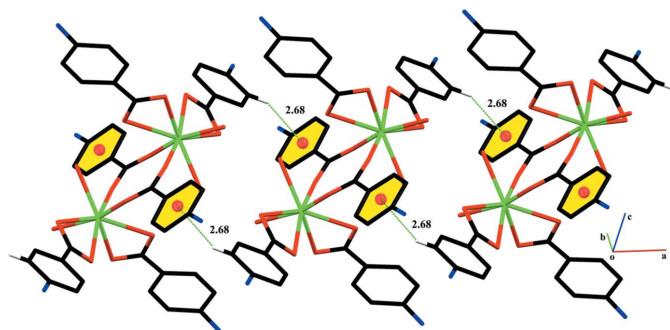


Figure 3
Graphical representation of C–H... π interactions in **4ABA-Tm**. Selected H atoms are shown while the water molecules are omitted for clarity.

direction is formed through O7–H7A...N3 H bonds while a loop is formed through the O7–H7A...N3 interactions. The water molecule of crystallization plays an important role in the stabilization of the crystal packing, acting as a hydrogen-bond donor and as well as a hydrogen-bond acceptor, connecting the centrosymmetric dinuclear thulium complex with each other. The hydrogen bonds lead to the formation of layers parallel to the *bc* plane (Fig. 2, Table 2). These layers are linked through C–H... π (Fig. 3), with H... π distance of 2.68 Å and off-set π – π stacking interactions (Fig. 4) with inter-centroid distances ranging from 3.661 (3) to 3.709 (3) Å, forming a three-dimensional network.

4. Hirshfeld surface analysis

A Hirshfeld surface (HS) analysis was carried out using *Crystal Explorer 21.5* (Spackman *et al.*, 2021) in order to explore the non-covalent interactions in terms of the Hirshfeld surface and two-dimensional fingerprint plots. The HS of a molecule is the region in the crystal where the electron density relevant to the promolecule is greater than the electron density relevant to the procrystal (Spackman *et al.*, 2009; Ashfaq *et al.*, 2020). The Hirshfeld surface is constructed by

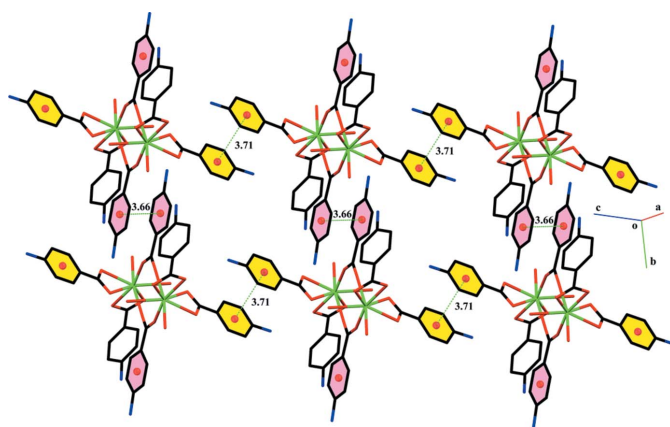


Figure 4
Graphical representation of off-set π – π interactions in **4ABA-Tm**. H atoms and water molecules are not shown for simplicity.

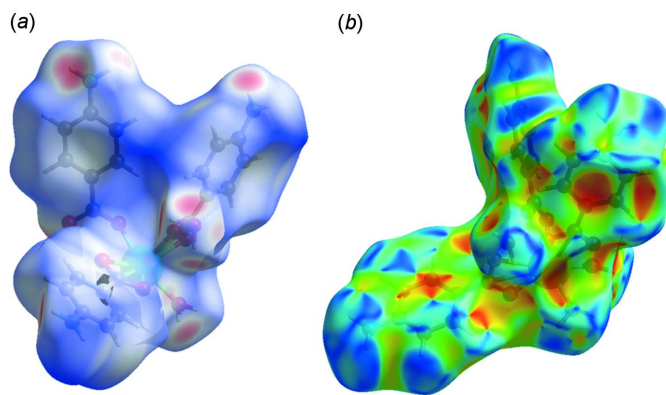


Figure 5
HS plotted over (a) d_{norm} in the range -1.073 to 1.740 a.u. and (b) shape-index in the range -1 to 1 a.u.

employing colour coding to show the interatomic contacts that are shorter (red areas), equal to (white areas), or longer than (blue areas) the sum of the van der Waals radii (Ashfaq *et al.*, 2021*a,b*). The red spots on the surface mapped over d_{norm} (Fig. 5*a*) indicate the involvement of atoms in hydrogen-bonding interactions. The HS mapped over shape-index (Fig. 5*b*) is used to check for the presence of interactions such as C–H... π and π – π stacking (Ashfaq *et al.*, 2021*a,b*). The existence of adjacent red and blue triangular regions around the aromatic rings conforms to the presence of π – π stacking interactions in the title compound.

Two-dimensional fingerprint plots provide unique information about the non-covalent interactions and the crystal packing in terms of the percentage contribution of the interatomic contacts (Spackman *et al.*, 2002; Ashfaq *et al.*, 2021*a,b*). Fig. 6*a* shows the two-dimensional fingerprint plot for the overall interactions in **4ABA-Tm** where d_i and d_e are the distances from the Hirshfeld surface to the nearest atom inside and outside it, respectively. The most

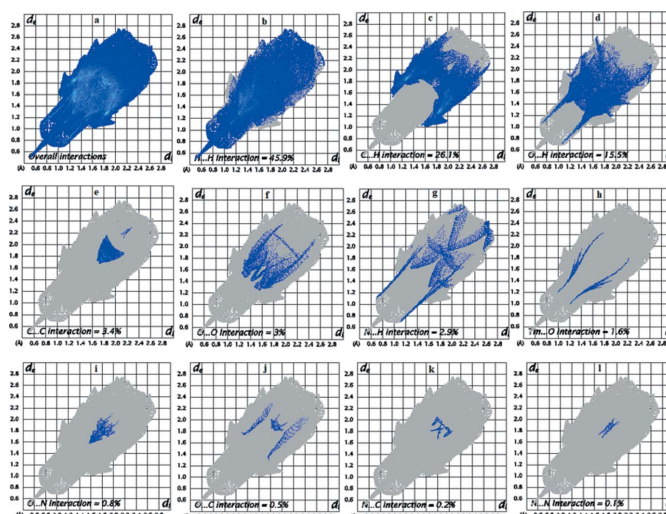


Figure 6
Two-dimensional fingerprint plots of **4ABA-Tm** for (a) all interactions and (b)–(l) individual interatomic contacts.

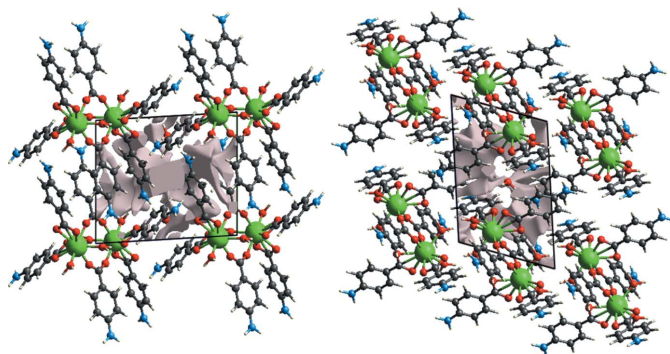


Figure 7
Graphical representation of **4ABA-Tm** in (a) a view along the *a* axis and (b) a view along the *b* axis.

important interatomic contact is $\text{H}\cdots\text{H}$ (Fig. 6*b*) as it makes the highest contribution to the crystal packing (45.9%). Other major contributors are $\text{C}\cdots\text{H}$ (26.1%, Fig. 6*c*) and $\text{O}\cdots\text{H}$ (15.5%, Fig. 6*d*) interactions. The interatomic contacts that make comparatively smaller contributions in the crystal packing are shown in Fig. 6*e–l*.

The response to applied stress or force mainly depends on the strength of the crystal packing in single crystals, which have a high mechanical strength as the molecules are strongly packed into them. To check whether the title compound is mechanically stable or not, a void analysis was performed. In order to calculate voids in the crystal packing, the electron densities of all of the atoms in the molecules present in the asymmetric unit are added up, the atoms being assumed to be spherically symmetric (Turner *et al.*, 2011; Kargar *et al.*, 2022). The volume of the void in the crystal packing of the title compound is 120.81 \AA^3 (Fig. 7), which infers that voids occupy 10.51% of the space and, hence, the molecules are strongly packed in the title compound.

5. Infra-red spectroscopy

The structure of the newly synthesized complex was also investigated by FT-IR spectroscopy. It was found that the absorption bands of the $-\text{NH}_2$ group appeared in the region of 3200 cm^{-1} while the absorption bands due to $\text{Tm}-\text{OH}_2$ are visible in the region of 325 cm^{-1} . The aromatic carbons show their absorption band at 1225 cm^{-1} , while the $\text{Tm}-\text{O}$ band is visible in the region of 650 cm^{-1} . The absorption bands observed in the FT-IR spectrum of the free ligand in the regions of 1715 and 1435 cm^{-1} are caused by symmetric (ν_s) and asymmetric (ν_{as}) stretching of the carboxyl group, which are shifted to 1635 and 1436 cm^{-1} , respectively, upon coordination with the Tm^{III} metal ion. The difference between ν_s and ν_{as} is 199 cm^{-1} , indicating that the carboxyl groups are coordinated to the central metal ion by chelate and bidentate-bridging coordination modes.

6. Thermogravimetric analysis

The title complex was further characterized by thermogravimetry. Thermolysis occurs in three stages. In the first

stage, at a temperature of $20\text{--}200^\circ\text{C}$, intermolecular and coordinated water molecules are released, with a weight loss of 4.69%. The complex remains stable over the temperature $200\text{--}400^\circ\text{C}$. In the second stage, at a temperature of $400\text{--}600^\circ\text{C}$, the hydrocarbon residues are decomposed and simultaneously burned out. Thulium carbonate is formed in the last stage at a temperature between 600 and 800°C . The final product of decomposition above 800°C is metal oxide.

It is known that lanthanide carboxylates have good spectroscopic characteristics; they have enhanced thermal stability and are also resistant to moisture and oxygen in the air, which is of great importance in the production and operation of photoluminescent and electroluminescent devices based on them.

7. Database survey

A search of the Cambridge Structural Database (CSD, version 5.40; update February 2021; Groom *et al.*, 2016) gave 206 hits, some of whose crystal structures are closely related to **4ABA-Tm**. These include the yttrium (NADYEX), holmium (NADZAU), lutetium (NADZIC) and ytterbium (YENRAK01) complexes reported by Sun *et al.* (2004). Erbium (YUTNAE; Smith & Lynch, 2015) and terbium (NADXEWO1; Ye *et al.*, 2004) complexes were also found in the literature.

8. Synthesis and crystallization

The infra-red spectrum of **4ABA-Tm** in the range 4000 to 250 cm^{-1} was recorded on an FT-IR Prestige 21 spectrophotometer after preparing the samples with KBr pellets. Thermal analysis was carried out using a NETSCHSTA-409 PC/PG derivatograph, TG, DTG and DTA curves were obtained in a static air atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ from $20\text{--}800^\circ\text{C}$ using platinum crucibles. Highly sintered Al_2O_3 was used as a reference. The elemental analysis for C, H, and N was performed using a Costech ECS 4010 CHNSO analyzer.

Preparation of the title complex

The reaction of aqueous solutions of TmCl_3 and sodium *p*-aminobenzoate (1:3) yielded single crystals of tris(*p*-aminobenzoato)thulium(III) dihydrate suitable for X-ray diffraction analysis. The mixture was refluxed for 30 minutes and then cooled to room temperature. After filtration, the filtrate was left for several days, covered with aluminum foil, until yellow prismatic crystals appeared. $\text{C}_{42}\text{H}_{48}\text{N}_6\text{O}_{18}\text{Tm}_2$, *M*: $1262.72 \text{ g mol}^{-1}$. Elemental analysis: calculated %: C:41.11; N: 6.25; Tm: 27.57; found %: C:41.24; N:6.72; Tm: 27.41.

9. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms of all the water molecules and the amino groups of 4-aminobenzoate ligands were found by the careful inspection of residual electron-density peaks and positional parameters were refined using bond-length

Table 3
Experimental details.

Crystal data	
Chemical formula	C ₄₂ H ₄₈ N ₆ O ₁₈ Tm ₂
<i>M</i> _r	1262.72
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.9659 (6), 10.9722 (7), 12.8027 (8)
α , β , γ (°)	88.195 (3), 71.599 (3), 74.402 (3)
<i>V</i> (Å ³)	1149.10 (13)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.92
Crystal size (mm)	0.32 × 0.18 × 0.16
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause et al., 2015)
<i>T</i> _{min} – <i>T</i> _{max}	0.983, 0.986
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	13239, 4891, 4358
<i>R</i> _{int}	0.037
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.639
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.064, 1.04
No. of reflections	4891
No. of parameters	343
No. of restraints	19
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.80, -1.07

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), *ORTEP-3 for Windows WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2020).

restraints (O–H = 0.82 Å, N–H = 0.85 Å) with *U*_{iso}(H) = 1.5*U*_{eq}(O) or 1.2*U*_{eq}(N). All other H atoms were refined at calculated positions using a riding-model approximation [C–H = 0.93 Å, *U*_{iso}(H) = 1.2*U*_{eq}(C)]. The highest positive and negative features in the final difference map are within 0.83 Å of the Tm atom.

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supporting information

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Synthesis, crystal structure, Hirshfeld surface and void analysis of bis(μ_2 -4-aminobenzoato- $\kappa^2O:O'$)bis[bis(4-aminobenzoato- κ^2O,O')diaquathulium(III)] dihydrate

Kasumova Samira Ali, Muhammad Ashfaq, Muhammad Nawaz Tahir, Elman Muhammad Movsumov and Khurram Shahzad Munawar

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2020).

Bis(μ_2 -4-aminobenzoato- $\kappa^2O:O'$)bis[bis(4-aminobenzoato- κ^2O,O')diaquathulium(III)] dihydrate

Crystal data

$C_{42}H_{48}N_6O_{18}Tm_2$
 $M_r = 1262.72$
 Triclinic, $P\bar{1}$
 $a = 8.9659$ (6) Å
 $b = 10.9722$ (7) Å
 $c = 12.8027$ (8) Å
 $\alpha = 88.195$ (3)°
 $\beta = 71.599$ (3)°
 $\gamma = 74.402$ (3)°
 $V = 1149.10$ (13) Å³

$Z = 1$
 $F(000) = 624$
 $D_x = 1.825$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 4358 reflections
 $\theta = 2.5$ – 27.0 °
 $\mu = 3.92$ mm⁻¹
 $T = 296$ K
 Prism, light yellow
 $0.32 \times 0.18 \times 0.16$ mm

Data collection

Bruker Kappa APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: 7.828 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan
 (SADABS; Krause et al., 2015)
 $T_{\min} = 0.983$, $T_{\max} = 0.986$

13239 measured reflections
 4891 independent reflections
 4358 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\max} = 27.0$ °, $\theta_{\min} = 2.5$ °
 $h = -11 \rightarrow 9$
 $k = -11 \rightarrow 14$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.064$

$S = 1.04$
 4891 reflections
 343 parameters
 19 restraints

Primary atom site location: structure-invariant direct methods
 Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0257P)^2 + 0.6134P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.80 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.07 \text{ e } \text{\AA}^{-3}$

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 $F^2 > \sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Tm1	0.63601 (2)	-0.01205 (2)	0.13511 (2)	0.02731 (7)
O1	0.3377 (4)	0.0164 (3)	0.2017 (2)	0.0380 (7)
O2	0.4938 (4)	-0.1008 (3)	0.2892 (2)	0.0458 (8)
O3	0.6097 (4)	0.1341 (3)	0.2770 (2)	0.0468 (8)
O4	0.8365 (3)	0.1015 (2)	0.1382 (2)	0.0351 (6)
O5	0.5346 (4)	0.1682 (3)	0.0675 (3)	0.0518 (9)
O6	0.3957 (5)	0.1706 (3)	-0.0479 (3)	0.0601 (10)
O7	0.8305 (4)	-0.1673 (3)	0.1803 (3)	0.0469 (8)
H7A	0.9297 (15)	-0.183 (4)	0.164 (4)	0.056*
H7B	0.801 (5)	-0.221 (3)	0.221 (3)	0.056*
O8	0.8252 (4)	-0.0313 (3)	-0.0465 (2)	0.0372 (7)
H8A	0.783 (5)	-0.034 (4)	-0.094 (3)	0.045*
H8B	0.9240 (14)	-0.053 (4)	-0.077 (3)	0.045*
N1	-0.1604 (7)	-0.2330 (6)	0.5608 (4)	0.0795 (16)
H1A	-0.163 (7)	-0.258 (6)	0.625 (2)	0.095*
H1B	-0.248 (4)	-0.193 (6)	0.549 (5)	0.095*
N2	0.8267 (6)	0.6323 (4)	0.3384 (3)	0.0520 (11)
H2A	0.922 (3)	0.629 (5)	0.340 (4)	0.062*
H2B	0.753 (4)	0.677 (4)	0.393 (3)	0.062*
N3	0.1667 (6)	0.7572 (3)	0.1054 (4)	0.0595 (12)
H3A	0.184 (7)	0.781 (5)	0.162 (3)	0.071*
H3B	0.209 (6)	0.792 (5)	0.049 (2)	0.071*
C1	0.3548 (6)	-0.0615 (4)	0.2755 (3)	0.0342 (9)
C2	0.2186 (6)	-0.1081 (4)	0.3440 (3)	0.0350 (9)
C3	0.0591 (6)	-0.0550 (4)	0.3473 (3)	0.0407 (10)
H3	0.0364	0.0097	0.3013	0.049*
C4	-0.0683 (6)	-0.0961 (5)	0.4179 (4)	0.0502 (12)
H4	-0.1752	-0.0594	0.4191	0.060*
C5	-0.0343 (7)	-0.1938 (5)	0.4876 (4)	0.0576 (15)

C6	0.1255 (7)	-0.2498 (5)	0.4815 (4)	0.0558 (13)
H6	0.1497	-0.3172	0.5248	0.067*
C7	0.2475 (6)	-0.2070 (4)	0.4126 (4)	0.0474 (11)
H7	0.3544	-0.2449	0.4110	0.057*
C8	0.7365 (5)	0.1669 (4)	0.2249 (3)	0.0330 (9)
C9	0.7643 (5)	0.2844 (4)	0.2605 (3)	0.0315 (9)
C10	0.9155 (5)	0.3092 (4)	0.2208 (3)	0.0349 (9)
H10	1.0038	0.2487	0.1744	0.042*
C11	0.9373 (6)	0.4220 (4)	0.2489 (3)	0.0370 (10)
H11	1.0401	0.4360	0.2225	0.044*
C12	0.8074 (6)	0.5145 (4)	0.3160 (3)	0.0379 (10)
C13	0.6544 (6)	0.4907 (4)	0.3559 (3)	0.0421 (11)
H13	0.5658	0.5524	0.4006	0.051*
C14	0.6336 (6)	0.3768 (4)	0.3299 (3)	0.0379 (10)
H14	0.5318	0.3614	0.3588	0.046*
C15	0.4332 (5)	0.2238 (3)	0.0213 (4)	0.0347 (9)
C16	0.3553 (5)	0.3619 (3)	0.0476 (3)	0.0260 (8)
C17	0.3834 (5)	0.4241 (4)	0.1289 (3)	0.0359 (10)
H17	0.4461	0.3781	0.1700	0.043*
C18	0.3196 (6)	0.5536 (4)	0.1497 (4)	0.0425 (11)
H18	0.3377	0.5938	0.2056	0.051*
C19	0.2295 (5)	0.6232 (3)	0.0884 (4)	0.0377 (10)
C20	0.1950 (6)	0.5613 (4)	0.0106 (4)	0.0431 (11)
H20	0.1283	0.6070	-0.0280	0.052*
C21	0.2592 (5)	0.4313 (4)	-0.0104 (3)	0.0372 (10)
H21	0.2370	0.3908	-0.0642	0.045*
O9	0.4466 (6)	0.1607 (6)	0.5070 (4)	0.0969 (15)
H9A	0.499 (8)	0.146 (6)	0.4401 (15)	0.116*
H9B	0.491 (9)	0.094 (4)	0.532 (5)	0.116*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tm1	0.03208 (11)	0.02149 (9)	0.02871 (10)	-0.00610 (7)	-0.01104 (7)	-0.00037 (6)
O1	0.0419 (18)	0.0381 (15)	0.0329 (15)	-0.0097 (13)	-0.0122 (13)	0.0087 (12)
O2	0.0425 (19)	0.0590 (19)	0.0446 (18)	-0.0195 (16)	-0.0225 (15)	0.0214 (15)
O3	0.054 (2)	0.0528 (18)	0.0336 (17)	-0.0295 (16)	-0.0005 (15)	-0.0096 (14)
O4	0.0367 (17)	0.0360 (14)	0.0327 (15)	-0.0106 (13)	-0.0096 (13)	-0.0083 (12)
O5	0.049 (2)	0.0259 (14)	0.071 (2)	-0.0004 (14)	-0.0142 (17)	0.0154 (14)
O6	0.061 (2)	0.0425 (18)	0.074 (2)	-0.0184 (17)	-0.0109 (19)	-0.0271 (17)
O7	0.0337 (18)	0.0453 (18)	0.061 (2)	-0.0087 (15)	-0.0182 (17)	0.0238 (15)
O8	0.0377 (17)	0.0431 (16)	0.0277 (15)	-0.0052 (14)	-0.0104 (13)	-0.0040 (12)
N1	0.096 (4)	0.106 (5)	0.052 (3)	-0.064 (4)	-0.014 (3)	0.014 (3)
N2	0.077 (3)	0.0324 (19)	0.047 (2)	-0.025 (2)	-0.012 (2)	-0.0010 (17)
N3	0.047 (3)	0.0211 (17)	0.087 (3)	-0.0036 (17)	0.006 (2)	-0.0008 (19)
C1	0.045 (3)	0.0304 (19)	0.028 (2)	-0.0130 (18)	-0.0115 (18)	0.0008 (16)
C2	0.041 (3)	0.035 (2)	0.032 (2)	-0.0134 (19)	-0.0137 (18)	0.0021 (17)
C3	0.046 (3)	0.050 (3)	0.032 (2)	-0.025 (2)	-0.011 (2)	0.0033 (19)

C4	0.042 (3)	0.073 (3)	0.042 (3)	-0.027 (3)	-0.012 (2)	-0.005 (2)
C5	0.086 (4)	0.069 (3)	0.033 (3)	-0.055 (3)	-0.010 (3)	-0.001 (2)
C6	0.071 (4)	0.058 (3)	0.052 (3)	-0.032 (3)	-0.029 (3)	0.019 (2)
C7	0.052 (3)	0.047 (3)	0.047 (3)	-0.018 (2)	-0.018 (2)	0.010 (2)
C8	0.040 (2)	0.037 (2)	0.025 (2)	-0.0137 (19)	-0.0115 (18)	0.0023 (16)
C9	0.041 (2)	0.0311 (19)	0.026 (2)	-0.0114 (18)	-0.0125 (17)	-0.0005 (15)
C10	0.041 (3)	0.033 (2)	0.029 (2)	-0.0115 (18)	-0.0075 (18)	-0.0031 (16)
C11	0.045 (3)	0.040 (2)	0.029 (2)	-0.020 (2)	-0.0084 (19)	0.0022 (17)
C12	0.064 (3)	0.0270 (19)	0.027 (2)	-0.018 (2)	-0.016 (2)	0.0047 (16)
C13	0.052 (3)	0.030 (2)	0.036 (2)	-0.006 (2)	-0.006 (2)	-0.0047 (17)
C14	0.043 (3)	0.041 (2)	0.028 (2)	-0.014 (2)	-0.0059 (18)	-0.0004 (17)
C15	0.031 (2)	0.0228 (18)	0.045 (2)	-0.0109 (17)	-0.0009 (18)	-0.0006 (17)
C16	0.029 (2)	0.0219 (17)	0.0278 (19)	-0.0073 (15)	-0.0100 (16)	-0.0011 (14)
C17	0.041 (3)	0.031 (2)	0.038 (2)	-0.0037 (18)	-0.0210 (19)	0.0019 (17)
C18	0.044 (3)	0.036 (2)	0.050 (3)	-0.011 (2)	-0.017 (2)	-0.013 (2)
C19	0.035 (2)	0.0201 (17)	0.050 (3)	-0.0087 (17)	-0.0014 (19)	0.0031 (17)
C20	0.043 (3)	0.039 (2)	0.043 (3)	-0.002 (2)	-0.016 (2)	0.0157 (19)
C21	0.044 (3)	0.040 (2)	0.030 (2)	-0.0086 (19)	-0.0168 (19)	0.0002 (17)
O9	0.067 (3)	0.148 (5)	0.066 (3)	-0.019 (3)	-0.016 (2)	0.010 (3)

Geometric parameters (Å, °)

Tm1—O5	2.216 (3)	C3—C4	1.388 (6)
Tm1—O6 ⁱ	2.223 (3)	C3—H3	0.9300
Tm1—O7	2.293 (3)	C4—C5	1.405 (7)
Tm1—O2	2.329 (3)	C4—H4	0.9300
Tm1—O3	2.374 (3)	C5—C6	1.376 (6)
Tm1—O8	2.382 (3)	C6—C7	1.355 (7)
Tm1—O4	2.457 (3)	C6—H6	0.9300
Tm1—O1	2.471 (3)	C7—H7	0.9300
Tm1—C1	2.774 (4)	C8—C9	1.488 (5)
Tm1—C8	2.781 (4)	C9—C10	1.387 (6)
O1—C1	1.272 (5)	C9—C14	1.397 (5)
O2—C1	1.270 (5)	C10—C11	1.379 (5)
O3—C8	1.262 (5)	C10—H10	0.9300
O4—C8	1.275 (5)	C11—C12	1.383 (6)
O5—C15	1.253 (5)	C11—H11	0.9300
O6—C15	1.251 (5)	C12—C13	1.397 (6)
O6—Tm1 ⁱ	2.223 (3)	C13—C14	1.377 (6)
O7—H7A	0.817 (10)	C13—H13	0.9300
O7—H7B	0.816 (10)	C14—H14	0.9300
O8—H8A	0.820 (10)	C15—C16	1.487 (5)
O8—H8B	0.819 (10)	C16—C21	1.375 (5)
N1—C5	1.381 (7)	C16—C17	1.383 (5)
N1—H1A	0.847 (10)	C17—C18	1.381 (5)
N1—H1B	0.850 (10)	C17—H17	0.9300
N2—C12	1.399 (5)	C18—C19	1.372 (6)
N2—H2A	0.850 (10)	C18—H18	0.9300

N2—H2B	0.850 (10)	C19—C20	1.378 (6)
N3—C19	1.423 (5)	C20—C21	1.387 (6)
N3—H3A	0.851 (10)	C20—H20	0.9300
N3—H3B	0.842 (10)	C21—H21	0.9300
C1—C2	1.467 (6)	O9—H9A	0.832 (10)
C2—C3	1.379 (6)	O9—H9B	0.835 (10)
C2—C7	1.397 (6)		
O5—Tm1—O6 ⁱ	108.53 (13)	O1—C1—C2	121.6 (4)
O5—Tm1—O7	156.90 (13)	O2—C1—Tm1	56.5 (2)
O6 ⁱ —Tm1—O7	84.40 (13)	O1—C1—Tm1	62.9 (2)
O5—Tm1—O2	125.29 (12)	C2—C1—Tm1	171.2 (3)
O6 ⁱ —Tm1—O2	81.97 (13)	C3—C2—C7	117.4 (4)
O7—Tm1—O2	74.42 (11)	C3—C2—C1	122.8 (4)
O5—Tm1—O3	80.05 (12)	C7—C2—C1	119.8 (4)
O6 ⁱ —Tm1—O3	161.28 (12)	C2—C3—C4	121.4 (4)
O7—Tm1—O3	93.61 (13)	C2—C3—H3	119.3
O2—Tm1—O3	79.58 (11)	C4—C3—H3	119.3
O5—Tm1—O8	78.30 (11)	C3—C4—C5	119.4 (5)
O6 ⁱ —Tm1—O8	74.11 (12)	C3—C4—H4	120.3
O7—Tm1—O8	87.42 (11)	C5—C4—H4	120.3
O2—Tm1—O8	151.26 (11)	C6—C5—N1	120.8 (5)
O3—Tm1—O8	124.48 (11)	C6—C5—C4	119.2 (5)
O5—Tm1—O4	80.34 (11)	N1—C5—C4	120.0 (6)
O6 ⁱ —Tm1—O4	142.65 (11)	C7—C6—C5	120.2 (5)
O7—Tm1—O4	78.06 (11)	C7—C6—H6	119.9
O2—Tm1—O4	123.35 (10)	C5—C6—H6	119.9
O3—Tm1—O4	53.82 (10)	C6—C7—C2	122.3 (5)
O8—Tm1—O4	72.41 (10)	C6—C7—H7	118.8
O5—Tm1—O1	75.80 (11)	C2—C7—H7	118.8
O6 ⁱ —Tm1—O1	76.29 (11)	O3—C8—O4	119.1 (4)
O7—Tm1—O1	126.75 (11)	O3—C8—C9	120.4 (4)
O2—Tm1—O1	54.20 (10)	O4—C8—C9	120.4 (4)
O3—Tm1—O1	90.29 (10)	O3—C8—Tm1	58.3 (2)
O8—Tm1—O1	131.47 (10)	O4—C8—Tm1	62.0 (2)
O4—Tm1—O1	139.92 (9)	C9—C8—Tm1	166.2 (3)
O5—Tm1—C1	101.68 (12)	C10—C9—C14	118.4 (4)
O6 ⁱ —Tm1—C1	75.71 (12)	C10—C9—C8	121.6 (4)
O7—Tm1—C1	100.03 (12)	C14—C9—C8	119.8 (4)
O2—Tm1—C1	27.06 (11)	C11—C10—C9	121.1 (4)
O3—Tm1—C1	86.36 (11)	C11—C10—H10	119.4
O8—Tm1—C1	148.00 (11)	C9—C10—H10	119.4
O4—Tm1—C1	139.52 (10)	C10—C11—C12	120.6 (4)
O1—Tm1—C1	27.28 (10)	C10—C11—H11	119.7
O5—Tm1—C8	75.79 (12)	C12—C11—H11	119.7
O6 ⁱ —Tm1—C8	169.50 (13)	C11—C12—C13	118.7 (4)
O7—Tm1—C8	88.48 (13)	C11—C12—N2	120.6 (4)
O2—Tm1—C8	103.56 (11)	C13—C12—N2	120.6 (4)

O3—Tm1—C8	26.88 (11)	C14—C13—C12	120.7 (4)
O8—Tm1—C8	97.92 (11)	C14—C13—H13	119.7
O4—Tm1—C8	27.29 (11)	C12—C13—H13	119.7
O1—Tm1—C8	114.19 (11)	C13—C14—C9	120.5 (4)
C1—Tm1—C8	113.24 (12)	C13—C14—H14	119.8
C1—O1—Tm1	89.8 (3)	C9—C14—H14	119.8
C1—O2—Tm1	96.4 (2)	O6—C15—O5	123.8 (4)
C8—O3—Tm1	94.8 (2)	O6—C15—C16	117.8 (4)
C8—O4—Tm1	90.7 (2)	O5—C15—C16	118.4 (4)
C15—O5—Tm1	145.2 (3)	C21—C16—C17	118.6 (3)
C15—O6—Tm1 ⁱ	157.5 (3)	C21—C16—C15	121.1 (3)
Tm1—O7—H7A	134 (3)	C17—C16—C15	120.3 (3)
Tm1—O7—H7B	118 (3)	C18—C17—C16	120.9 (4)
H7A—O7—H7B	108 (4)	C18—C17—H17	119.6
Tm1—O8—H8A	113 (3)	C16—C17—H17	119.6
Tm1—O8—H8B	139 (3)	C19—C18—C17	120.3 (4)
H8A—O8—H8B	106 (3)	C19—C18—H18	119.8
C5—N1—H1A	126 (4)	C17—C18—H18	119.8
C5—N1—H1B	107 (5)	C18—C19—C20	119.1 (4)
H1A—N1—H1B	120 (4)	C18—C19—N3	121.7 (4)
C12—N2—H2A	114 (4)	C20—C19—N3	119.2 (4)
C12—N2—H2B	116 (3)	C19—C20—C21	120.5 (4)
H2A—N2—H2B	111 (4)	C19—C20—H20	119.8
C19—N3—H3A	109 (4)	C21—C20—H20	119.8
C19—N3—H3B	110 (4)	C16—C21—C20	120.5 (4)
H3A—N3—H3B	112 (4)	C16—C21—H21	119.7
O2—C1—O1	119.0 (4)	C20—C21—H21	119.7
O2—C1—C2	119.4 (4)	H9A—O9—H9B	100 (4)
Tm1—O2—C1—O1	-8.3 (4)	C14—C9—C10—C11	0.1 (6)
Tm1—O2—C1—C2	170.8 (3)	C8—C9—C10—C11	175.8 (4)
Tm1—O1—C1—O2	7.8 (4)	C9—C10—C11—C12	-1.2 (6)
Tm1—O1—C1—C2	-171.3 (3)	C10—C11—C12—C13	0.9 (6)
O2—C1—C2—C3	168.9 (4)	C10—C11—C12—N2	-175.6 (4)
O1—C1—C2—C3	-12.0 (6)	C11—C12—C13—C14	0.6 (6)
O2—C1—C2—C7	-8.5 (6)	N2—C12—C13—C14	177.1 (4)
O1—C1—C2—C7	170.6 (4)	C12—C13—C14—C9	-1.8 (6)
C7—C2—C3—C4	1.5 (6)	C10—C9—C14—C13	1.4 (6)
C1—C2—C3—C4	-176.0 (4)	C8—C9—C14—C13	-174.4 (4)
C2—C3—C4—C5	0.1 (7)	Tm1 ⁱ —O6—C15—O5	23.7 (11)
C3—C4—C5—C6	-2.4 (7)	Tm1 ⁱ —O6—C15—C16	-157.9 (6)
C3—C4—C5—N1	178.0 (5)	Tm1—O5—C15—O6	-34.8 (8)
N1—C5—C6—C7	-177.3 (5)	Tm1—O5—C15—C16	146.8 (4)
C4—C5—C6—C7	3.1 (8)	O6—C15—C16—C21	-6.8 (6)
C5—C6—C7—C2	-1.5 (8)	O5—C15—C16—C21	171.7 (4)
C3—C2—C7—C6	-0.8 (7)	O6—C15—C16—C17	175.6 (4)
C1—C2—C7—C6	176.7 (4)	O5—C15—C16—C17	-5.9 (6)
Tm1—O3—C8—O4	-12.7 (4)	C21—C16—C17—C18	-1.5 (7)

Tm1—O3—C8—C9	164.0 (3)	C15—C16—C17—C18	176.2 (4)
Tm1—O4—C8—O3	12.2 (4)	C16—C17—C18—C19	-1.2 (7)
Tm1—O4—C8—C9	-164.5 (3)	C17—C18—C19—C20	4.0 (7)
O3—C8—C9—C10	166.1 (4)	C17—C18—C19—N3	-177.9 (4)
O4—C8—C9—C10	-17.3 (6)	C18—C19—C20—C21	-4.1 (7)
Tm1—C8—C9—C10	-113.5 (12)	N3—C19—C20—C21	177.8 (4)
O3—C8—C9—C14	-18.2 (6)	C17—C16—C21—C20	1.4 (6)
O4—C8—C9—C14	158.4 (4)	C15—C16—C21—C20	-176.2 (4)
Tm1—C8—C9—C14	62.2 (13)	C19—C20—C21—C16	1.4 (7)

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

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

Cg3 is the centroid of the C16–C21 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7—H7A \cdots N3 ⁱⁱ	0.82 (1)	1.95 (2)	2.753 (6)	169 (5)
O7—H7B \cdots N2 ⁱⁱⁱ	0.82 (1)	2.18 (2)	2.940 (5)	154 (5)
O8—H8A \cdots O1 ⁱ	0.82 (1)	1.98 (1)	2.791 (4)	172 (4)
O8—H8B \cdots O4 ^{iv}	0.82 (1)	1.96 (1)	2.780 (4)	174 (4)
N1—H1B \cdots O9 ^v	0.85 (1)	2.06 (3)	2.870 (8)	158 (7)
N2—H2B \cdots O9 ^{vi}	0.85 (1)	2.24 (2)	3.051 (7)	161 (5)
N3—H3B \cdots O5 ^{vii}	0.84 (1)	2.46 (3)	3.173 (6)	144 (5)
N3—H3B \cdots O8 ^{vii}	0.84 (1)	2.56 (5)	3.092 (5)	122 (4)
O9—H9A \cdots O3	0.83 (1)	2.00 (1)	2.828 (6)	172 (7)
O9—H9B \cdots O2 ^{viii}	0.84 (1)	2.34 (6)	2.849 (6)	119 (5)
C11—H11 \cdots Cg3 ^{ix}	0.93	2.68	3.538 (5)	155

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