

2,2',2''-Nitrilotris(ethylammonium) tris(pyridine-2,6-dicarboxylato- $\kappa^3O,N,O'$ )terbate(III) hexahydrateLin Chen,<sup>a</sup> Xian-Hong Yin,<sup>b†</sup>  
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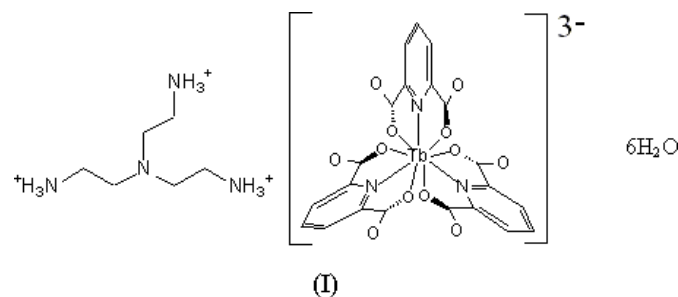
## Key indicators

Single-crystal X-ray study  
 $T = 296\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$   
H-atom completeness 79%  
 $R$  factor = 0.033  
 $wR$  factor = 0.089  
Data-to-parameter ratio = 12.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The asymmetric unit of the title compound,  $(\text{C}_6\text{H}_{21}\text{N}_4)\text{[Tb}(\text{C}_7\text{H}_3\text{NO}_4)_3\cdot 6\text{H}_2\text{O}]$ , consists of a  $(\text{C}_6\text{H}_{21}\text{N}_4)^{3+}$  cation, and a  $[\text{C}_7\text{H}_3\text{NO}_4)_3\text{Tb}]^{3-}$  anion, and six molecules of water. In the anion, three pyridine-2,6-dicarboxylate ligands are coordinated to the  $\text{Tb}^{\text{III}}$  atom *via* the N atom of the pyridine ring and two O atoms of different carboxylate groups. The coordination polyhedron around Tb may be described as a pseudo-tricapped trigonal prism. The crystal packing is stabilized by electrostatic interactions and intermolecular hydrogen bonds involving the cation, anion and water molecules.

## Comment

Pyridine-2,6-dicarboxylic acid ( $\text{H}_2\text{pdc}$ ) exhibits biological activity (Pocker & Fong, 1980; Scapin *et al.*, 1997). The crystal structure of  $\text{H}_2\text{pdc}\cdot\text{H}_2\text{O}$  has been known for many years (Takusagawa *et al.*, 1973). It is also a versatile ligand, known to coordinate as a neutral, monobasic or dibasic chelating agent and function as a bidentate, bridging or meridional tridentate ligand (Gielen *et al.*, 1987; Preut *et al.*, 1988; Chessa *et al.*, 1991; Håkansson *et al.*, 1993; Lainé *et al.*, 1995; Koman *et al.*, 2000; Nathan & Mai, 2000; Okabe & Oya, 2000; Matković-Čalogović *et al.*, 2002). As part of our studies on rare-earth complexes of  $\text{H}_2\text{pdc}$ , we present the crystal structure of the title complex, 2,2',2''-nitrilotris(ethylammonium) tris(pyridine-2,6-dicarboxylato)terbate(III) hexahydrate, (I).



The asymmetric unit of (I) consists of a  $[\text{Tb}(\text{pdc})_3]^{3-}$  anion, a  $(\text{C}_6\text{H}_{21}\text{N}_4)^{3+}$  cation and six water molecules (Fig. 1). The C—O distances involving the coordinated O atoms [1.260 (5)–1.290 (5) Å] are longer than those involving the uncoordinated O atoms [1.229 (6)–1.244 (5) Å] (Table 1). A discrete trigonal prism is formed by two triangles, defined by two sets of carboxylate O atoms (O1/O5/O11) and (O3/O7/O9). Atoms N1, N2 and N3 cap the discrete trigonal prism to form a discrete tricapped trigonal prism. Atoms Tb, N1, N2 and N3 are nearly coplanar, with Tb having the largest deviation, of 0.013 (1) Å. The bond angles around the central N atom (N4) of the  $(\text{C}_6\text{H}_{21}\text{N}_4)^{3+}$  cation vary from 110.3 (4) to 112.7 (4)° and the sum of the angles [334.6 (4)°] indicates that the N atom is

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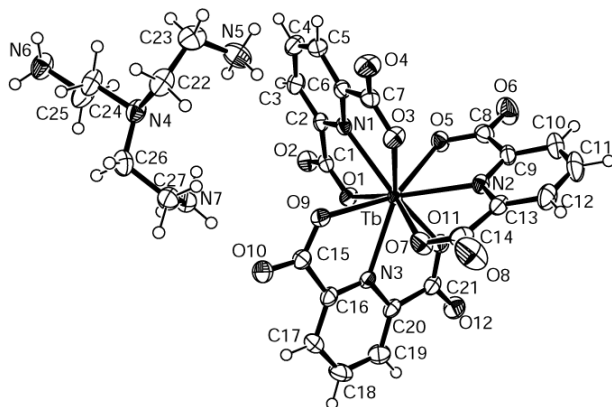


Figure 1

A view of the molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 40% probability level. Solvent water molecules have been omitted for clarity.

in a pyramidal configuration. The crystal structure is stabilized by N—H···O and O—H···O hydrogen bonds involving the cation, anion and solvent water molecules (Table 2). Short intermolecular O···O contacts less than 3 Å, involving the solvent water O atoms, range from 2.722 (6) to 2.889 (9) Å.

## Experimental

A mixture of Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, tri(2-aminoethyl)amine and H<sub>2</sub>pdc (molar ratio 1:1:3) in water–ethanol (1:1 v/v) was neutralized with aqueous NH<sub>3</sub>·H<sub>2</sub>O to pH = 7, and then refluxed with stirring at 333 K for 3 h. The resulting solution was left to stand at room temperature and allowed to evaporate slowly over a period of a few days for crystallization. Crystals of the title compound suitable for X-ray diffraction analysis were collected by filtration, washed with ethanol and dried in air.

### Crystal data

(C <sub>6</sub> H <sub>21</sub> N <sub>4</sub> )[Tb(C <sub>7</sub> H <sub>3</sub> NO <sub>4</sub> ) <sub>3</sub> ]·6H <sub>2</sub> O	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 911.60	<i>D<sub>x</sub></i> = 1.761 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 10.538 (2) Å	Cell parameters from 38 reflections
<i>b</i> = 12.068 (3) Å	<i>θ</i> = 4.1–15.5°
<i>c</i> = 15.747 (3) Å	<i>μ</i> = 2.15 mm <sup>-1</sup>
<i>α</i> = 87.31 (1)°	<i>T</i> = 296 (2) K
<i>β</i> = 71.24 (2)°	Triclinic, colorless
<i>γ</i> = 65.66 (2)°	0.58 × 0.58 × 0.48 mm
<i>V</i> = 1719.1 (6) Å <sup>3</sup>	

### Data collection

Siemens P4 diffractometer	<i>R</i> <sub>int</sub> = 0.070
<i>ω</i> scans	<i>θ</i> <sub>max</sub> = 25.0°
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>h</i> = 0 → 12
<i>T</i> <sub>min</sub> = 0.795, <i>T</i> <sub>max</sub> = 0.951	<i>k</i> = -13 → 14
6350 measured reflections	<i>l</i> = -17 → 18
6011 independent reflections	3 standard reflections
5440 reflections with <i>I</i> > 2σ( <i>I</i> )	every 97 reflections
	intensity decay: 6.6%

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H atoms treated by a mixture of independent and constrained refinement
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.033	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F<sub>o</sub></i> <sup>2</sup> ) + (0.0686 <i>P</i> ) <sup>2</sup> ]
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.089	where <i>P</i> = ( <i>F<sub>o</sub></i> <sup>2</sup> + 2 <i>F<sub>c</sub></i> <sup>2</sup> )/3
<i>S</i> = 1.03	(Δ/ <i>σ</i> ) <sub>max</sub> = 0.001
6011 reflections	Δ <i>ρ</i> <sub>max</sub> = 2.42 e Å <sup>-3</sup>
493 parameters	Δ <i>ρ</i> <sub>min</sub> = -1.24 e Å <sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Tb—O7	2.393 (3)	O3—C7	1.260 (5)
Tb—O3	2.398 (3)	O4—C7	1.244 (5)
Tb—O9	2.428 (3)	O5—C8	1.290 (5)
Tb—O1	2.431 (3)	O6—C8	1.229 (6)
Tb—O11	2.435 (3)	O7—C14	1.261 (5)
Tb—O5	2.448 (3)	O8—C14	1.236 (6)
Tb—N1	2.492 (3)	O9—C15	1.264 (5)
Tb—N3	2.499 (3)	O10—C15	1.239 (5)
Tb—N2	2.508 (3)	O11—C21	1.268 (5)
O1—C1	1.265 (5)	O12—C21	1.235 (5)
O2—C1	1.243 (5)		
O7—Tb—O3	76.76 (11)	O5—Tb—N1	73.52 (10)
O7—Tb—O9	75.65 (11)	O7—Tb—N3	71.48 (11)
O3—Tb—O9	78.48 (10)	O3—Tb—N3	135.41 (11)
O7—Tb—O1	145.15 (10)	O9—Tb—N3	64.02 (10)
O3—Tb—O1	127.82 (10)	O1—Tb—N3	74.02 (11)
O9—Tb—O1	85.11 (10)	O11—Tb—N3	64.31 (10)
O7—Tb—O11	92.44 (11)	O5—Tb—N3	135.46 (11)
O3—Tb—O11	148.33 (10)	N1—Tb—N3	123.68 (10)
O9—Tb—O11	128.12 (10)	O7—Tb—N2	63.94 (11)
O1—Tb—O11	76.83 (10)	O3—Tb—N2	72.80 (10)
O7—Tb—O5	128.33 (10)	O9—Tb—N2	134.45 (11)
O3—Tb—O5	88.92 (11)	O1—Tb—N2	140.41 (11)
O9—Tb—O5	149.74 (10)	O11—Tb—N2	75.70 (10)
O1—Tb—O5	81.12 (10)	O5—Tb—N2	64.39 (10)
O11—Tb—O5	74.46 (10)	N1—Tb—N2	118.99 (11)
O7—Tb—N1	135.31 (11)	N3—Tb—N2	117.31 (11)
O3—Tb—N1	64.06 (10)	C26—N4—C22	111.6 (4)
O9—Tb—N1	76.23 (10)	C26—N4—C24	112.7 (4)
O1—Tb—N1	63.99 (10)	C22—N4—C24	110.3 (4)
O11—Tb—N1	132.23 (10)		
N4—C22—C23—N5	-71.4 (5)	N4—C26—C27—N7	-62.7 (5)
N4—C24—C25—N6	-179.1 (4)		

Table 2

Hydrogen-bonding 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>
O13—H13A···O5	0.82 (4)	2.10 (3)	2.880 (5)	158 (8)
O14—H14A···O18	0.82 (5)	2.02 (5)	2.789 (8)	157 (3)
O16—H16A···O9	0.83 (7)	2.01 (7)	2.837 (5)	178 (8)
N7—H7B···O10	0.89	1.97	2.855 (5)	174
N5—H5A···O4 <sup>i</sup>	0.89	2.19	2.979 (6)	147
N5—H5B···O17 <sup>i</sup>	0.89	2.15	2.971 (7)	152
N5—H5C···O2 <sup>ii</sup>	0.89	1.97	2.851 (5)	171
N6—H6C···O12 <sup>iii</sup>	0.89	1.96	2.840 (5)	172
N6—H6B···O11 <sup>ii</sup>	0.89	2.12	2.960 (5)	158
N6—H6A···O15 <sup>ii</sup>	0.89	2.44	2.838 (5)	107
N7—H7C···O2 <sup>ii</sup>	0.89	1.98	2.851 (5)	165
N7—H7A···O13 <sup>ii</sup>	0.89	2.13	2.977 (6)	160

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

Only three H atoms of the water molecules were located from successive difference Fourier maps and they were refined isotropically with restrained bond lengths. H atoms of the pyridine ring and (C<sub>6</sub>H<sub>21</sub>N<sub>4</sub>)<sup>3+</sup> moiety were positioned geometrically and refined using a riding model, with C—H = 0.93 Å for pyridine, N—H = 0.89 Å and C—H = 0.97 Å for the (C<sub>6</sub>H<sub>21</sub>N<sub>4</sub>)<sup>3+</sup> moiety, and with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub> of the parent atoms. The highest peak and deepest hole in the final difference map were located at distances less than 1.1 Å from the Tb atom.

Data collection: XSCANS (Siemens, 1991); cell refinement: XSCANS; data reduction: SHELXTL (Sheldrick, 1997a); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s)

used to refine structure: *SHELXL97* (Sheldrick, 1997b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

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