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Key indicators

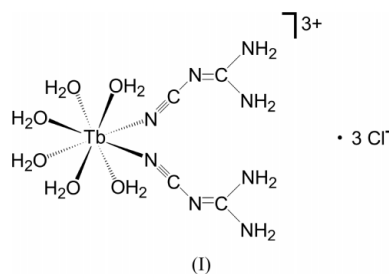
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{N}-\text{C}) = 0.007\text{ \AA}$
 R factor = 0.022
 wR factor = 0.055
Data-to-parameter ratio = 15.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Hexaaquabis(dicyanoguanidine)terbium(III)
trichloride

In the title compound, $[\text{Tb}(\text{C}_2\text{H}_4\text{N}_4)_2(\text{H}_2\text{O})_6]\text{Cl}_3$, the coordination of the terbium(III) ion is a square-antiprismatic arrangement by six O atoms and two monodentate cyanoguanidine (cng) molecules forming covalent Tb—N bonds of 2.446 (4) Å through their nitrile N atoms. The crystal structure consists of metal ion layers separated by the organic molecules along the a axis.

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Comment

As a commercially important compound, cyanoguanidine (cng) or dicyandiamide, the dimeric form of cyanamide (H_2NCN), is a versatile precursor for the synthesis of organonitrogen compounds. The coordination chemistry of this species has been the object of considerable attention. In most cases, it acts as a neutral monodentate ligand, binding to the metal through its cyano N atom only. There are some complexes with transition metals such as copper(II) (Ammar *et al.*, 2002; Batsanov *et al.*, 1997), copper(I) (Batsanov *et al.*, 1996), zinc(II) (Harrison *et al.*, 2001; Pickardt & Kühn, 1996a), silver(I) (Dronskowski & Liu, 2003; Bessler *et al.*, 2003), cadmium(II) and mercury(II) Pickardt & Kühn, 1996b). However, until now, there have been no reports on rare earth-cng complexes. We report here the structure of such a complex, *viz.* the title compound, (I) (Fig. 1).



The Tb atom is eight-coordinated by two cng and six water molecules. The structure is a distorted square-antiprism (D_{4d}), with the distortions due mainly to the difference in the Tb—O and Tb—N distances. The cng ligand coordinates the Tb atom *via* its nitrile N atom, with a Tb—N distance of 2.446 (4) Å. Typical distances for Tb—N bonds are 2.38–2.62 Å (Allen, 2002). The values of the geometric parameters for (I) (Table 1) are reasonable, when considering similar internuclear interactions in other eight-coordinate Tb species (Bell & Smith, 1990). In the present compound, two cng molecules substitute the two coordinated chloride anions of $[\text{Tb}(\text{H}_2\text{O})_6\text{Cl}_2]\text{Cl}$.

The hydrogen bonds are listed in Table 2. The cng molecule is a hydrogen-bonding ligand that may act as a donor

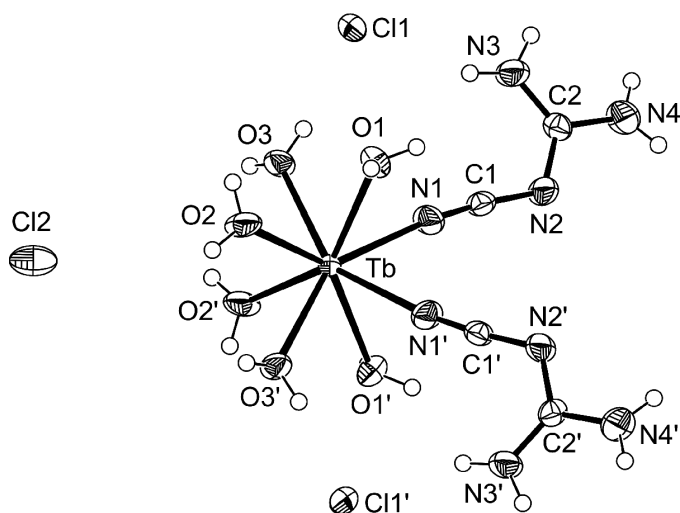


Figure 1
Molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level for non-H atoms [symmetry code: (i) $-x, -y, z$].

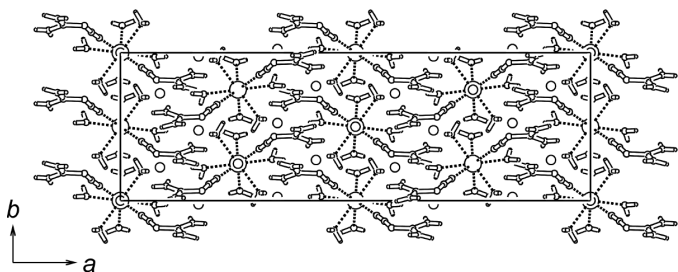


Figure 2
Crystal packing of the title compound, viewed down the c axis.

(amino, NH_2) and as an acceptor (cyanimino, $\text{=N-C}\equiv\text{N}$). In this compound, the N–H donor systems from the amino group have close contacts to the chloride anions. The hydrogen bonding between the water molecules and the chloride anions ($\text{O-H}\cdots\text{Cl}$ interactions) is indicated by short $\text{O}\cdots\text{Cl}$ distances of 3.03–3.16 Å (Pimental & McClellan, 1960). There is also hydrogen bonding (2.79 Å) between the imino N atom and the water molecule ($\text{N2}\cdots\text{O2}$).

The cngc molecule is essentially planar and the maximum distance from the least-squares plane is 0.014 Å. The coordination does not severely affect the structural parameters of cngc (Fernanda *et al.*, 1993). The structure as a whole consists of layers stacked along the a direction (shown in Fig. 2) and the distance between two metal layers is 7.356 (1) Å. The organic molecules (cngc) separate and stabilize the metal ion layers.

Experimental

The title compound was prepared using the rheological method (semi-solid phase reaction; Zhang *et al.*, 1999). For a traditional synthesis, TbCl_3 [1.6 mmol, obtained by dissolving 0.30 g Tb_4O_7 (Aldrich, 99.99%) in concentrated HCl and evaporating the excess acid], H_2NCN (cyanamide, Aldrich, 99%; 0.1 g, 2.4 mmol) and appropriate amount of water were mixed into a semi-solid phase and sealed in a glass bottle. After two months, some colourless crystals

with strong green luminescence under UV radiation were obtained. On the other hand, the sample obtained by slow evaporation of a solution of TbCl_3 and H_2NCN was simply dicyandiamide [$\text{NCNC}(\text{NH}_2)_2$].

Crystal data

$[\text{Tb}(\text{C}_2\text{H}_4\text{N}_4)_2(\text{H}_2\text{O})_6]\text{Cl}_3$
 $M_r = 541.55$
 Orthorhombic, $Fdd2$
 $a = 29.425$ (5) Å
 $b = 9.2613$ (14) Å
 $c = 13.690$ (2) Å
 $V = 3730.6$ (10) Å³
 $Z = 8$
 $D_x = 1.928$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 6486 reflections
 $\theta = 2.7$ – 28.3°
 $\mu = 4.26$ mm⁻¹
 $T = 293$ (2) K
 Prism, colourless
 $0.31 \times 0.08 \times 0.05$ mm

Data collection

Bruker AXS APEX CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.290$, $T_{\max} = 0.808$
 6486 measured reflections

2185 independent reflections
 2065 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -39 \rightarrow 39$
 $k = -12 \rightarrow 8$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.055$
 $S = 1.10$
 2185 reflections
 142 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0315P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.43$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.60$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.00174 (7)
 Absolute structure: Flack (1983),
 980 Friedel pairs
 Flack parameter = -0.030 (13)

Table 1

Selected geometric parameters (Å, °).

Tb–O1	2.432 (3)	Tb–O3	2.374 (3)
Tb–O2	2.356 (4)	Tb–N1	2.446 (4)
O2 ⁱ –Tb–O2	93.0 (3)	O3–Tb–N1	76.55 (13)
O3 ⁱ –Tb–O3	131.88 (17)	O1–Tb–N1	74.50 (11)
O1–Tb–O1 ⁱ	140.49 (16)	N1–Tb–N1 ⁱ	83.32 (19)
O2–Tb–N1	139.99 (12)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O1–H11 \cdots Cl1 ⁱⁱ	0.82 (2)	2.34 (2)	3.156 (3)	174 (6)
O1–H12 \cdots Cl2	0.82 (2)	2.36 (3)	3.141 (3)	159 (8)
O2–H21 \cdots N2 ⁱⁱⁱ	0.82 (2)	2.00 (3)	2.785 (5)	160 (6)
O2–H22 \cdots Cl1 ^{iv}	0.82 (2)	2.29 (4)	3.077 (3)	159 (8)
O3–H31 \cdots Cl1 ^v	0.81 (2)	2.31 (2)	3.117 (4)	172 (6)
O3–H32 \cdots Cl1	0.81 (2)	2.23 (2)	3.033 (3)	171 (7)
N3–H33 \cdots Cl2 ^{vi}	0.853 (19)	2.49 (2)	3.306 (4)	161 (4)
N3–H34 \cdots Cl1	0.86 (2)	2.43 (3)	3.243 (5)	159 (5)
N4–H41 \cdots Cl2 ^{vi}	0.86 (2)	2.71 (5)	3.480 (5)	149 (7)
N4–H42 \cdots O1 ^{vii}	0.85 (2)	2.67 (3)	3.492 (6)	161 (6)

Symmetry codes: (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (iii) $x, \frac{1}{2} + y, z - \frac{1}{2}$; (iv) $x - \frac{1}{4}, \frac{1}{4} - y, z - \frac{1}{4}$; (v) $\frac{1}{4} - x, y - \frac{1}{4}, z - \frac{1}{4}$; (vi) $\frac{1}{4} + x, \frac{1}{4} - y, \frac{1}{4} + z$; (vii) $x, y - \frac{1}{2}, \frac{1}{2} + z$.

The initial positions of all H atoms were determined from difference Fourier maps and these atoms were refined isotropically. Due to some short N–H and O–H distances (less than 0.8 Å), we applied a soft restraint for all N–H and O–H bond lengths (0.86 Å for N–H

and 0.82 Å for O—H; Sheldrick, 1998). The final refinement gave reasonable hydrogen-bond lengths and connectivities.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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