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Key indicators

Single-crystal X-ray study
 T = 200 K
 Mean $\sigma(C-C)$ = 0.005 Å
 R factor = 0.028
 wR factor = 0.083
 Data-to-parameter ratio = 16.5

For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

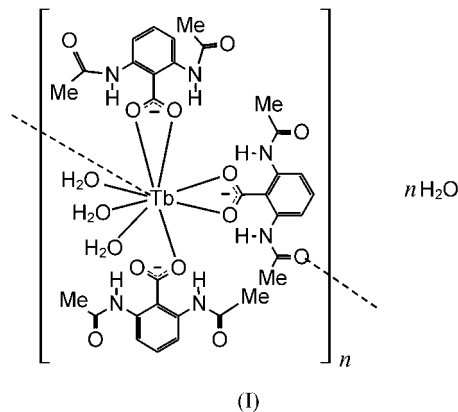
catena-Poly[[[triquabis(2,6-diacetamido-
 benzoato)terbium(III)]- μ -2,6-diacetamido-
 benzoato] monohydrate]

The title compound, $\{[Tb(C_{11}H_{11}N_2O_4)_3(H_2O)_3] \cdot H_2O\}_n$, has a Tb ion coordinated by bulky benzoate ligands. The Tb ion coordination sphere is occupied by nine O atoms, five from benzoate groups, three from water molecules and one from an amide carbonyl group of a neighboring ligand. Five amide NH groups of the three ligands are involved in intramolecular N—H···O hydrogen bonds.

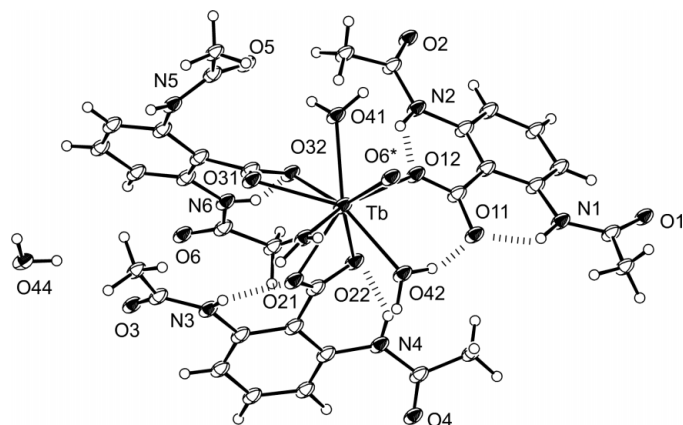
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Comment

Hydrogen bonds to metal-coordinating atoms are frequently found in the active sites of metalloproteins and we have focused on the roles of the conserved N—H···O hydrogen bonds to carboxylate groups and the relationship with their binding properties (Ueyama *et al.*, 1998, 1999, 2001; Yamada *et al.*, 1998; Onoda *et al.*, 2001; Onoda, Yamada, Okamura, Yamamoto & Ueyama, 2002; Onoda, Yamada, Okamura, Doi *et al.*, 2002; Onoda, Yamada, Takeda *et al.*, 2004; Onoda, Yamada, Nakayama *et al.*, 2004; Takahashi *et al.*, 2004). We have reported Ca^{II} and Tb^{III} complexes with benzoate ligands having bulky amide substituents in the *ortho* positions, *viz.* 2,6-(^tBuCONH)₂C₆H₃CO₂H. This ligand has stable intramolecular six-membered N—H···O hydrogen bonds, forming six-membered rings; it also prevents the formation of polymeric complexes as a result of steric congestion. Thus, we have obtained mononuclear homoleptic Ca^{II} and Tb^{III} complexes with three or four carboxylate ligands. We have studied in detail the effect of the N—H···O hydrogen bonds on the Ca^{II} ion binding with the carboxylate in a solution using Tb^{III} ions as fluorescence probes in aqueous solution, using the less bulky 2,6-(MeCONH)₂C₆H₃CO₂H.



We report here the crystal structure of a Tb^{III} complex with the 2,6-(MeCONH)₂C₆H₃CO₂H ligand. The title compound, (I) (Fig. 1), has a Tb^{III} ion surrounded by nine O atoms, five from benzoate groups, three from water molecules and one

**Figure 1**

View of the title complex, showing the labeling of selected non-H atoms and 30% probability displacement ellipsoids.

from an amide carbonyl group of a neighboring ligand (Table 1). Two benzoate ligands coordinate Tb in a chelate bidentate fashion and the third benzoate ligand coordinates in a monodentate fashion. The uncoordinated carboxylate O atom is hydrogen-bonded to the water ligated to the Tb^{III} ion. Five amide NH groups of the three ligands are involved in intramolecular N—H...O hydrogen bonds, forming six-membered rings (Table 2). The amide N5—H5 group, which is free from involvement in an intramolecular N—H...O hydrogen bond, interacts with the neighboring amide carbonyl O2 atom. The amide C=O5 group forms intermolecular hydrogen bonds with atoms O41 and O43.

Experimental

The synthesis of the title compound has been reported previously (Onoda, Yamada, Okamura, Doi *et al.*, 2002). Crystals were obtained by recrystallization from hot acetonitrile.

Crystal data

[Tb(C ₁₁ H ₁₁ N ₂ O ₄) ₃ (H ₂ O) ₃].H ₂ O	$D_x = 1.662 \text{ Mg m}^{-3}$
$M_r = 936.64$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 31087 reflections
$a = 9.4505(2) \text{ \AA}$	$\theta = 1.5\text{--}27.5^\circ$
$b = 28.9468(8) \text{ \AA}$	$\mu = 1.97 \text{ mm}^{-1}$
$c = 13.7255(2) \text{ \AA}$	$T = 200 \text{ K}$
$\beta = 94.608(1)^\circ$	Block, colorless
$V = 3742.63(14) \text{ \AA}^3$	$0.20 \times 0.20 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer	8325 independent reflections
ω scans	7077 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.053$
$T_{\text{min}} = 0.562$, $T_{\text{max}} = 0.675$	$\theta_{\text{max}} = 27.5^\circ$
32750 measured reflections	$h = -10 \rightarrow 12$
	$k = -37 \rightarrow 37$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.028$	$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2]$
$wR(F^2) = 0.083$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{\text{max}} = 0.001$
8325 reflections	$\Delta\rho_{\text{max}} = 0.71 \text{ e \AA}^{-3}$
505 parameters	$\Delta\rho_{\text{min}} = -1.03 \text{ e \AA}^{-3}$

Table 1

Selected bond distances (Å).

Tb—O12	2.373 (2)	Tb—O21	2.421 (2)
Tb—O43	2.380 (2)	Tb—O31	2.474 (2)
Tb—O41	2.381 (2)	Tb—O32	2.520 (2)
Tb—O42	2.416 (2)	Tb—O22	2.569 (2)
Tb—O6 ⁱ	2.420 (2)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N1—H1...O11	0.86	1.85	2.557 (3)	138
N2—H2...O12	0.86	1.90	2.602 (3)	138
N3—H3...O21	0.86	1.99	2.650 (3)	133
N4—H4...O22	0.86	1.98	2.674 (3)	137
N5—H5...O2 ⁱⁱ	0.86	1.98	2.831 (3)	172
N6—H6...O32	0.86	1.95	2.669 (3)	141
O41—H34...O5	0.82	2.02	2.822 (3)	164
O41—H35...O44 ⁱⁱⁱ	0.93	1.73	2.646 (3)	171
O42—H36...O4 ^{iv}	0.94	1.89	2.798 (3)	164
O42—H37...O11	0.93	1.79	2.663 (3)	157
O43—H39...O3 ⁱ	0.90	1.90	2.796 (3)	170
O43—H38...O5 ⁱⁱ	0.88	2.02	2.888 (2)	174
O44—H40...O1	0.91	1.85	2.722 (4)	160

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

The water H atoms were located in a difference Fourier map and included in the structure-factor calculations with fixed positional and isotropic displacement parameters. The remainder of the H atoms were positioned geometrically and were treated as riding on their parent C and N atoms, with aromatic C—H distances of 0.93 Å and amide N—H distances of 0.86 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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References

- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Onoda, A., Yamada, Y., Doi, M., Okamura, T. & Ueyama, N. (2001). *Inorg. Chem.* **40**, 516–521.
- Onoda, A., Yamada, Y., Nakayama, Y., Takahashi, K., Adachi, H., Okamura, T., Nakamura, A., Yamamoto, H., Ueyama, N., Vyprachticky, D. & Okamoto, Y. (2004). *Inorg. Chem.* **43**. In the press.

- Onoda, A., Yamada, Y., Okamura, T., Doi, M., Yamamoto, H. & Ueyama, N. (2002). *J. Am. Chem. Soc.* **124**, 1052–1059.
- Onoda, A., Yamada, Y., Okamura, T., Yamamoto, H. & Ueyama, N. (2002). *Inorg. Chem.* **41**, 6038–6047.
- Onoda, A., Yamada, Y., Takeda, J., Okamura, T., Doi, M., Yamamoto, H. & Ueyama, N. (2004). *Bull. Chem. Soc. Jpn*, **77**, 321–329.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Takahashi, K., Doi, M., Kobayashi, A., Tagushi, T., Onoda, A., Okamura, T., Yamamoto, H. & Ueyama, N. (2004). *Chem. Lett.* **33**, 192–193.
- Ueyama, N., Hosoi, T., Yamada, Y., Doi, M., Okamura, T. & Nakamura, A. (1998). *Macromolecules*, **31**, 7119–7126.
- Ueyama, N., Kozuki, H., Doi, M., Yamada, Y., Takahashi, K., Onoda, A., Okamura, T. & Yamamoto, H. (2001). *Macromolecules*, **34**, 2607–2614.
- Ueyama, N., Takeda, J., Yamada, Y., Onoda, A., Okamura, A. & Nakamura, A. (1999). *Inorg. Chem.* **38**, 475–478.
- Yamada, Y., Ueyama, N., Okamura, T., Mori, Y. & Nakamura, A. (1998). *Inorg. Chim. Acta*, **275–276**, 43–51.