Bis{6-methoxy-2-[(4-methylphenylimino)methyl]phenol-κ^2O,O'}tris(nitrato-κ^2O,O')-terbium(III) monohydrate

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The Tb atom in the title compound, [Tb(NO$_3$)$_3$(C$_{15}$H$_{15}$NO$_2$)$_2$]·H$_2$O, is coordinated by ten O atoms in a bicapped square-antiprismatic environment. The organic ligand assumes a zwitterionic form in chelating to the metal atom through two O atoms; the three nitrate groups also exhibit chelating behavior.

Comment

The crystal structures of a large number of metal complexes of Schiff bases that are derived by condensing substituted salicyaldehydes with amines have been reported (Cambridge Structural Database, Version 5.27 of November 2005; Allen, 2002). The reaction of o-vanillin with p-toluidine affords a Schiff base that rearranges its phenol H atom in its reaction with terbium(III) nitrate. The product, (I), has the Tb atom chelated by two of the zwitterionic Schiff base ligands (through the negatively charged phenol and methoxy O atoms) as well as by three nitrate groups (Fig. 1) in a geometry that is better described as a bicapped square antiprism. In the Schiff base ligand, the iminium unit forms an intramolecular hydrogen bond (Table 2) that probably forces it to assume a nearly planar conformation.

(I)
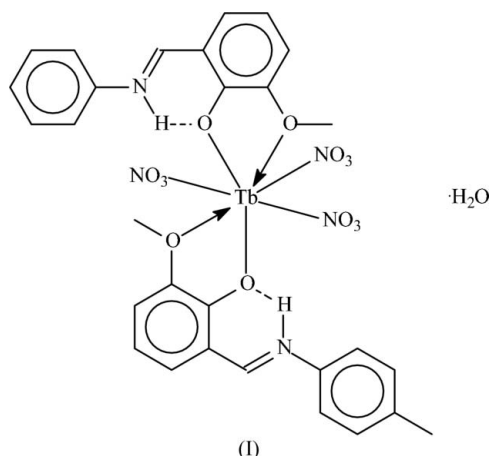
Experimental

To o-vanillin (1.52 g, 10 mmol) in methanol (20 ml) was added p-toluidine (1.07 g, 10 mmol) in methanol (20 ml) to give an orange solution; a solid product separated from the solution after 10 min. The product, collected in 80% yield (m.p. 373 K), was purified by recrystallization from ethanol. Analysis calculated for C$_{15}$H$_{15}$NO$_2$: C 74.66, H 6.27, N 5.81%; found: C 74.62, H 6.31, N 5.77%.

Terbium(III) nitrate hexahydrate was prepared by dissolving terbium oxide (Tb$_4$O$_7$, 99.95% purity) in concentrated nitric acid and

30% hydrogen peroxide (H_2O_2, 30%). The solution was concentrated on a steam bath to afford the hydrate. An ethanol solution (10 ml) of $Tb(NO_3)_3 \cdot 6H_2O$ (1.0 mmol, 0.45 g) was mixed with an ethanol solution (40 ml) of the Schiff base (2.0 mmol, 0.48 g); the mixture was heated for 3 h to give a clear red–orange solution. Red crystals were obtained from the cool solution after ten days. Calculated for $C_{30}H_{32}N_5O_{14}Tb$: C, 42.61, H 381, N 8.28, Tb 18.80%. Found C 42.94, H 3.80, N 8.29, Tb 19.12%.

Crystal data

$[Tb(NO_3)_3(C_{15}H_{15}NO_2)_2] \cdot H_2O$	$V = 1665.1$ (6) Å^3
$M_r = 845.53$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.686$ Mg m^{-3}
$a = 9.811$ (2) Å	Mo $K\alpha$ radiation
$b = 9.976$ (2) Å	$\mu = 2.20$ mm^{-1}
$c = 18.482$ (4) Å	$T = 293$ (2) K
$\alpha = 98.42$ (3)°	Block, red
$\beta = 101.54$ (3)°	$0.35 \times 0.09 \times 0.08$ mm
$\gamma = 105.90$ (3)°	

Data collection

Bruker APEX-II area-detector diffractometer	25200 measured reflections
	7537 independent reflections
φ and ω scans	6796 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.025$
	$\theta_{max} = 27.5°$
$T_{min} = 0.513$, $T_{max} = 0.844$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.6317P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.09$	$\Delta\rho_{max} = 0.64$ e Å^{-3}
7537 reflections	$\Delta\rho_{min} = -0.82$ e Å^{-3}
469 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected bond lengths (Å).

Tb1—O1	2.444 (3)	Tb1—O8	2.586 (3)
Tb1—O2	2.535 (3)	Tb1—O10	2.322 (2)
Tb1—O4	2.483 (2)	Tb1—O11	2.744 (2)
Tb1—O5	2.481 (3)	Tb1—O12	2.328 (2)
Tb1—O7	2.471 (3)	Tb1—O13	2.731 (2)

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1W-H2W \cdots O3$	0.87 (1)	1.98 (4)	2.817 (8)	161 (10)
$O1W-H1W \cdots O7^i$	0.86 (1)	2.36 (8)	3.007 (9)	132 (9)
$N4-H4N \cdots O10$	0.85 (1)	1.97 (3)	2.647 (4)	136 (3)
$N5-H5N \cdots O12$	0.84 (1)	1.90 (3)	2.584 (3)	137 (3)

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

The carbon-bound H atoms were positioned geometrically and refined using a riding model [C—H = 0.93–0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$]. The methyl groups were rotated to fit the electron density. The amino and water H atoms were located in a difference Fourier map and refined with N—H and O—H distance
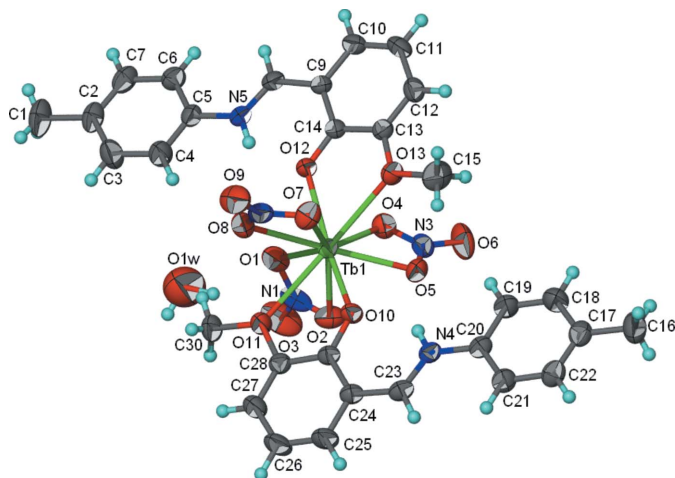

Figure 1
Molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms as spheres of arbitrary radii.
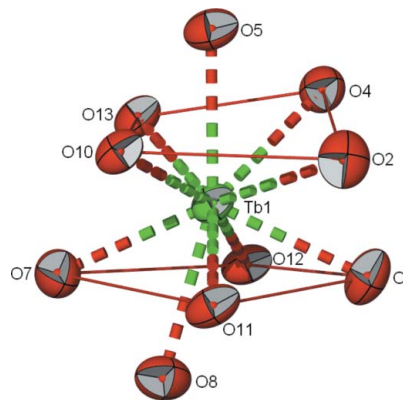

Figure 2
Ten-coordinate geometry of Tb.

restraints of 0.85 (1) Å and H$\cdots$H = 1.39 (1) Å; their displacement parameters were freely refined. The displacement parameter of the water O atom was restrained to be nearly isotropic.

Data collection: *APEXII* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2006).

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