

Aquachlorobis(4,4',4''-tri-*tert*-butyl-2,2';6',2''-terpyridine- κ^3N)terbium(III) diperchlorate ethanol disolvate

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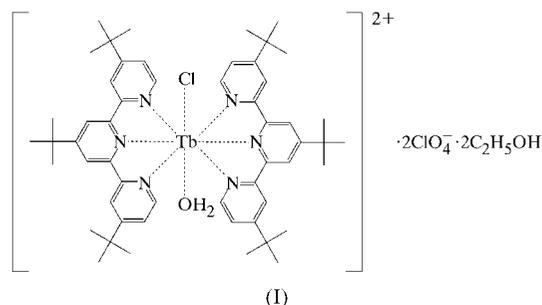
In the title compound, [TbCl(C₂₇H₃₅N₃)₂(H₂O)](ClO₄)₂·2C₂H₆O, the Tb^{III} ion has a coordination number of eight, composed of two tridentate substituted-terpyridine ligands, a water molecule and a bound Cl⁻ anion. The first coordination shell can be described as a distorted bicapped trigonal prism. The dihedral angles between pyridine rings belonging to the same tpy ligand range from 5.2 (5) to 16.8 (5)°.

Comment

As part of our ongoing research programme on lanthanide coordination compounds (Bünzli *et al.*, 2000), we are interested in the interplay between ligand structure and the photophysical properties of the complexes formed. Progress in these areas over the last two decades has led, for example, to the introduction of several commercially available fluoro-immunoassays based on highly luminescent lanthanide complexes (Hemmilä *et al.*, 1995; Mathis, 1998). We have recently shown (Mürner *et al.*, 2000) that the introduction of simple alkane substituents in the 4-positions of the parent compound 2,2';6',2''-terpyridine (tpy) greatly enhances the quantum yields of metal-centred luminescence in complexes with Eu^{III} and, particularly, with Tb^{III}. During our efforts to obtain X-ray quality crystals of the complexes [Ln(L¹)₃](ClO₄)₃ (where L¹ is 4,4',4''-tri-*tert*-butyl-2,2';6',2''-terpyridine), we obtained crystals that were comprised of the title compound, [Tb(L¹)₂(H₂O)Cl](ClO₄)₂·2C₂H₆O, (I), instead of the expected tris complex.

Complexes of the types [Ln(L)X₃] and [Ln(L)₃]³⁺ (where X is NO₃⁻ or a halogenide, and L is tpy or a derivative) have been reported in the literature with essentially all the rare earths. Recent examples are a series of papers by White (Semenova *et al.*, 1999; Semenova & White, 1999*a,b*), and work by Drew *et al.* (2000). Until very recently, only one X-ray structure of a complex in the lanthanide–tpy system displaying a 1:2 metal-to-ligand stoichiometry had been described. The

salt [La(tpy)₂(NO₃)₂][La(tpy)(NO₃)₄] contains a cationic species with ten-coordinate La^{III} and an anionic species with 11-coordinate La^{III} (Frechette & Bensimon, 1995). Structures of the analogous complexes [Ln(tpy)₂(NO₃)₂][Ln(tpy)(NO₃)₄] (Ln is Nd, Sm, Tb, Dy or Ho) have been reported recently (Drew *et al.*, 2000). In these compounds, both the cation and the anion display a coordination number of ten, with one of the four nitrate ligands in the anion binding only in a monodentate fashion. This contrasts with the La^{III} structure (Frechette & Bensimon, 1995), where all four nitrates act as bidentate ligands in the anion.



For the complexes [Ln(tpy)₂(NO₃)₂][Ln(tpy)(NO₃)₄] (Ln is La, Sm, Dy or Ho), dihedral angles between the pyridine rings of up to 29° were observed. For complexes where Ln is Tb or Nd, on the other hand, both tpy ligands are close to planarity (inter-pyridine angles < 10°). Large deviations from planarity in the ligands were also observed in the structures of [Ln(tpy)₃]³⁺ complexes (Skelton *et al.*, 1996; Semenova *et al.*, 1999). In contrast, the complex [TbCl(tpy)Cl(H₂O)₄]₂·3H₂O (Kepert *et al.*, 1994) displays dihedral angles of 9.4 and 10.6°. In the title compound, (I), the dihedral angles between pyridine rings in the same molecule of L¹ vary between 5.2 (5) and 16.8 (5)°. We conclude that, overall, the complexed ligand L¹ displays a nearly planar conformation. The reasons for the distortions in the tpy ligands bound to lanthanide cations remain unclear, especially if one considers the different behaviour displayed by neighbours in the series (*e.g.* Tb and Dy).

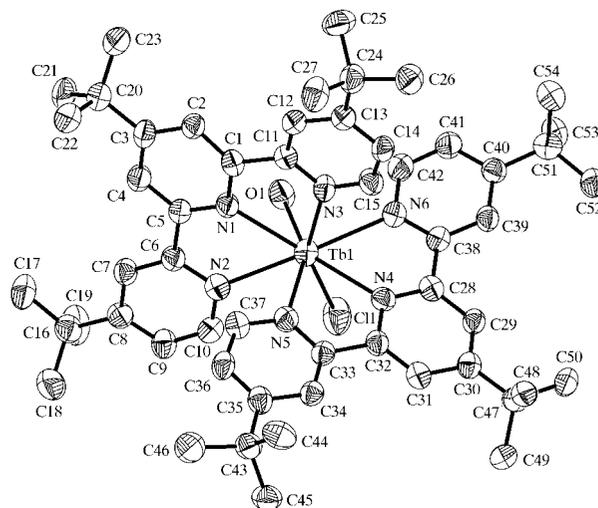


Figure 1

A view of the cation of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

All bond lengths between the central cation and the ligand atoms in (I) are comparable with those in the Tb^{III} mono-tpy complex (Kepert *et al.*, 1994). A noteworthy exception is that the bonds between the Tb and the N atoms of the two peripheral pyridine rings are not equal in (I). The observed Tb–N bonds are all slightly shorter than in the cation [Tb(tpy)₂(NO₃)₂]⁺ (Drew *et al.*, 2000), where non-equal bond lengths between Tb^{III} and peripheral pyridine N atoms are seen in only one of the tpy molecules. In contrast with other structures of rare earth complexes, (I) displays neither a mono- nor a bidentate binding of the perchlorate anions. Instead, a purely ionic behaviour is observed.

Hydrogen-bonding interactions are observed between the coordinated water and the ethanol solvate. Weaker interactions are apparent between the coordinated Cl and the ethanol solvate, and between perchlorate and C–H fragments of the pyridine rings. The coordination polyhedron for Tb^{III} can be described as a distorted bicapped trigonal prism (Porai-Koshits & Aslanov, 1972).

Experimental

The synthesis of and analytical data for the parent compound, [Tb(L¹)₃](ClO₄)₃, (II), have been described elsewhere (Mürner *et al.*, 2000). Suitable crystals of (I) formed upon slow evaporation of an MeCN–EtOH–pentane solution of (II) under non-anhydrous conditions. We attribute the presence of a Cl[−] counter-ion to the unintentional use of a solvent contaminated with traces of hydrochloric acid.

Crystal data

[TbCl(C ₂₇ H ₃₅ N ₃) ₂ (H ₂ O)]· (ClO ₄) ₂ ·2C ₂ H ₆ O	$D_x = 1.339 \text{ Mg m}^{-3}$
$M_r = 1306.58$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 708 reflections
$a = 14.392 (3) \text{ \AA}$	$\theta = 1.4\text{--}12.2^\circ$
$b = 21.233 (4) \text{ \AA}$	$\mu = 1.27 \text{ mm}^{-1}$
$c = 22.172 (4) \text{ \AA}$	$T = 143 (2) \text{ K}$
$\beta = 106.95 (3)^\circ$	Prismatic, colourless
$V = 6481 (2) \text{ \AA}^3$	$0.25 \times 0.20 \times 0.17 \text{ mm}$
$Z = 4$	

Data collection

MAR345 IPDS diffractometer	$R_{\text{int}} = 0.066$
φ scans ($\Delta\varphi = 3^\circ$; exposure time 180 s)	$\theta_{\text{max}} = 24.4^\circ$
34 863 measured reflections	$h = -16 \rightarrow 16$
10 324 independent reflections	$k = -24 \rightarrow 24$
5193 reflections with $I > 2\sigma(I)$	$l = -24 \rightarrow 25$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.065$	$w = 1/[\sigma^2(F_o^2) + (0.1083P)^2]$
$wR(F^2) = 0.203$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{\text{max}} = 0.001$
10 324 reflections	$\Delta\rho_{\text{max}} = 1.44 \text{ e \AA}^{-3}$
721 parameters	$\Delta\rho_{\text{min}} = -1.09 \text{ e \AA}^{-3}$

From refinement of the site occupancies, there was evidence that atoms Cl1 and O1 were disordered, but a satisfactory disordered model could not be obtained. One EtOH molecule was found to be disordered. A three-component model with isotropic displacement parameters was employed (occupancy factor 0.33 for all atoms). The H atoms of the solvent molecules and coordinated water were omitted. The remaining H atoms were placed in calculated positions and refined as riding, with C–H = 0.95–0.98 Å.

Table 1

Selected geometric parameters (Å, °).

Tb1–O1	2.383 (6)	Tb1–N1	2.515 (7)
Tb1–N3	2.503 (7)	Tb1–N6	2.531 (7)
Tb1–N4	2.506 (7)	Tb1–N2	2.558 (8)
Tb1–N5	2.510 (7)	Tb1–Cl1	2.633 (3)
O1–Tb1–N3	100.6 (2)	N1–Tb1–N6	127.9 (2)
O1–Tb1–N4	142.5 (2)	O1–Tb1–N2	75.5 (2)
N3–Tb1–N4	82.8 (2)	N3–Tb1–N2	128.1 (2)
O1–Tb1–N5	152.7 (2)	N4–Tb1–N2	131.2 (2)
N3–Tb1–N5	87.7 (2)	N5–Tb1–N2	78.9 (2)
N4–Tb1–N5	63.9 (2)	N1–Tb1–N2	64.2 (2)
O1–Tb1–N1	75.6 (2)	N6–Tb1–N2	147.7 (2)
N3–Tb1–N1	64.8 (2)	O1–Tb1–Cl1	85.52 (19)
N4–Tb1–N1	135.9 (2)	N3–Tb1–Cl1	151.87 (17)
N5–Tb1–N1	84.8 (2)	N4–Tb1–Cl1	76.22 (17)
O1–Tb1–N6	79.4 (2)	N5–Tb1–Cl1	99.41 (19)
N3–Tb1–N6	76.2 (2)	N1–Tb1–Cl1	142.61 (18)
N4–Tb1–N6	65.1 (2)	N6–Tb1–Cl1	78.08 (18)
N5–Tb1–N6	127.9 (2)	N2–Tb1–Cl1	80.07 (18)

Data collection: *MAR345 Software* (marresearch, 1999); cell refinement: *marHKL* (release 1.9.1), based on *HKL* (Otwinowski & Minor, 1997); data reduction: *marHKL*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1012). Services for accessing these data are described at the back of the journal.

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