Aquachlorobis(4,4′,4″-tri-tert-butyl-2,2′;6,2″-terpyridine-κ^3N)terbium(III) di perchlorate ethanol disolvate

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In the title compound, [TbCl(C_{27}H_{35}N_{3})_{2}(H_{2}O)][ClO_{4}]_{2}·2C_{2}H_{6}O, 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 fluorimunoassays based on highly luminescent lanthanide complexes (Hemmila 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(L')_{3}]·(ClO_{4})_{3} (where $L'$ is 4,4′,4″-tri-tert-butyl-2,2′;6,2″-terpyridine), we obtained crystals that were comprised of the title compound, [Tb(L')_{2}(H_{2}O)]Cl(ClO_{4})_{2}·2C_{2}H_{6}O, (1), instead of the expected tris complex.

Complexes of the types [Ln(L)X]_{1} and [Ln(L)X]^{1+} (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., 1999a; Semenova & White, 1999b), 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}(NO_{3})_{2}][La(tpy)(NO_{3})_{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)(NO_{3})_{4}]_{2}[Ln(tpy)(NO_{3})_{4}] (Ln is Nd, Sm, Tb, Dy or Ho) have been reported recently (Drew et al., 2000). In these complexes, 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 ligand.

For the complexes [Ln(tpy)_{2}(NO_{3})_{2}][Ln(tpy)(NO_{3})_{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+} complexes (Skelton et al., 1996; Semenova et al., 1999). In contrast, the complex [TbCl(tpy)Cl(H_{2}O)]_{2}·3H_{2}O (Keper 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 $L^{1}$ vary between 5.2 (5) and 16.8 (5)°. We conclude that, overall, the complexed ligand $L^{1}$ 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 are comparable with those in the TbIII 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)$_2$(NO$_3$)$_2$]$^+$(Drew et al., 2000), where non-equal bond lengths between TbIII 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 solvent Cl–H fragments of the pyridine rings. The coordination polyhedron for TbIII 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(L)$_3$(ClO$_4$)$_2$](II), have been described elsewhere (Münner et al., 2000). Suitable crystals of (I) formed upon slow evaporation of an MeCN–EtOH–pentane solution of (II) under non-anhydrous conditions. Suitable crystals of (I) formed upon slow evaporation of an MeCN–EtOH–pentane solution of (II) under non-anhydrous conditions. An exception is that a monoclinic, P2$_1$/c

Monoclinic, P2$_1$/c

- $a = 14.392$ (3) Å
- $b = 21.233$ (4) Å
- $c = 22.172$ (4) Å
- $\beta = 106.95$ (3)$^\circ$
- $V = 6481$ (2) Å$^3$
- $Z = 4$

#### Data collection

- MAR345 IPDS diffractometer
- $\theta$ scans ($\Delta \theta = 3^\circ$; exposure time $180\ s$)
- 34 863 measured reflections
- 10 324 independent reflections
- 5 193 reflections with $I > 2\sigma(I)$

#### Refinement

- Refined on $F^2$
- $R(F^2 > 2\sigma(F^2)) = 0.065$
- $wR(F^2) = 0.203$
- $S = 0.97$
- 30 242 reflections
- 721 parameters

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

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Data collection: MAR345 Software (marresearch, 1999); cell refinement: marHKL (release 1.9.1), based on HKL (Otwinski & 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.

### References


