metal-organic compounds

The twinned crystal structure of μ-2,2′-bipyrimidine-1κ^2N^1,$N^{1'}$: 2κ^2N^3,$N^{3'}$-bis{tris[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato-κ^2O,O']-terbium(III)} ethyl acetate solvate

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The title compound, [Tb$_2$(C$_{24}$H$_{12}$F$_9$O$_6$S$_3$)$_2$(C$_8$H$_6$N$_4$)]·C$_4$H$_8$O$_2$, has two terbium(III) centers bridged by the polyazine ligand 2,2′-bipyrimidine (bpm), which is distorted from planarity by 7.0 (2)°. The terminal ligand 4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dione (tta) is bidentate, coordinating through the two O atoms, while the bridging ligand is bis-bidentate, co-ordinating through four equivalent N atoms. Both the complex and the ethyl acetate solvent molecules are disordered. The structure was refined as a non-merohedral twin.

Comment

Terbium(III) ions and their complexes have been extensively used as probes for proteins and nucleic acids due, in part, to their long-lived (millisecond) excited-state lifetimes (Fu *et al.*, 1999; Klakamp & Horrocks, 1990). β-Diketonates are used as antenna ligands to overcome the forbidden 4f–4f transitions of lanthanide metals, thereby increasing the emission intensity of these complexes. Bridging ligands such as 2,2′-bipyrimidine (bpm) have been primarily used to link transition metals

(I)
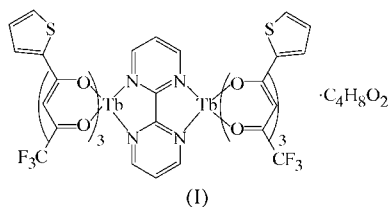
through coordination by equivalent N atoms (Balzani *et al.*, 1996). Heteronuclear bimetallic lanthanide/transition metal complexes bridged by bpm have been synthesized and structurally characterized (Shavaleev *et al.*, 2005). In these mixed-metal complexes, the planarity of the bpm bridging ligand is maintained and electronic communication between the two metal centers is observed. Examples of homodinuclear

lanthanide complexes bridged by bpm are rare (Sultan *et al.*, 2006). We present here the title compound, (I), in the first structural report of a homodinuclear Tb^{III} complex bridged by the polyazine ligand bpm.

Each Tb^{III} ion in (I) (Fig. 1) is eight-coordinate and the complex is neutral. Lanthanide(III) complexes, and particularly Tb^{III} complexes, are very often eight-coordinate due to the large ionic radius of the metal. The coordination sphere around each Tb^{III} ion consists of six O atoms from three 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (tta) ligands and two N atoms from the bpm ligand. Both Tb centers are in a distorted square-antiprismatic geometry, a coordination geometry previously reported in heteronuclear bimetallic lanthanide/transition metal complexes bridged by bpm (Shavaleev *et al.*, 2005). The approximate square planes at the Tb1 center are O5/O6/N1/N4 [average deviation = 0.306 (2) Å], and O1/O2/O3/O4 [average deviation = 0.300 (2) Å]. The corresponding approximate square planes at Tb2 are O9/O10/N2/N3 [average deviation = 0.131 (2) Å] and O7/O8/O11/O12 [average deviation = 0.045 (2) Å] (Fig. 1). These mean planes at the metal centers are nearly orthogonal, with a dihedral angle of 83.24 (6)° at Tb1, while the corresponding value at Tb2 is 89.87 (7)°.

The intramolecular Tb1···Tb2 distance across the bridging bpm ligand is 6.7596 (5) Å. The only other relevant Ln^{III}···Ln^{III} distance documented to date is in the bipyrimidine-bridged Eu^{III}···Eu^{III} complex reported by Fernandes *et al.* (2005), which has a metal–metal distance of 6.856 (1) Å. The longer distance in the Eu^{III} complex is consistent with the larger ionic radius of Eu^{III} compared with Tb^{III}, due to lanthanide contraction.

The individual bpm rings are planar, with a mean deviation of 0.003 (3) Å for atoms N1, C1, C2, C3, N2 and C4, and of 0.007 (3) Å for atoms N4, C5, N3, C6, C7 and C8; they are
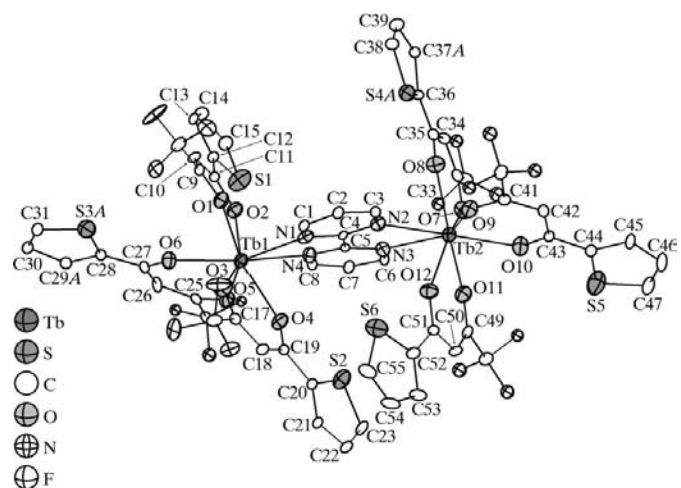

Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme for a single component of the disordered structure. For clarity, CF$_3$ groups have not been labeled. Displacement ellipsoids are drawn at the 20% probability level for C atoms and at 50% for all others. H atoms and the solvent molecule have been omitted for clarity.

rotated from planarity by 7.0 (2)°. In lanthanide–transition metal complexes bridged by bipyrimidine, the bridging ligand is planar (Shavaleev *et al.*, 2005). The unusual non-planarity observed in this complex is most likely due to the steric crowding of the bulky Tb^{III} ions forcing a slight torsional twist of the bridging ligand.

Part of both the solvent and the complex molecules are positionally disordered (see *Experimental*). Atom O13 of the solvent interacts weakly with the π system of the bpm ligand, based on the close O13···C4 and O13···C5 distances of 2.909 (7) and 2.799 (7) Å, respectively.

Experimental

The synthesis of the title Tb^{III} complex was accomplished as described previously by Sultan *et al.* (2006), by mixing the appropriate stoichiometries of an aqueous solution of $TbCl_3$ with a basic ethanolic solution containing bpm and tta. X-ray quality crystals were obtained by diffusion of hexanes into an ethyl acetate solution of the title Tb^{III} complex at room temperature.

Crystal data

[Tb₂(C₂₄H₁₂F₉O₆S₃)₂(C₈H₆N₄)]·· C₄H₈O₂	$Z = 2$
$M_r = 1891.14$	$D_x = 1.806$ Mg m⁻³
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.0301 (8)$ Å	Cell parameters from 4046
$b = 14.1408 (11)$ Å	reflections
$c = 24.9919 (9)$ Å	$\theta = 2.3–27.9°$
$\alpha = 85.820 (2)°$	$\mu = 2.31$ mm⁻¹
$\beta = 86.556 (2)°$	$T = 140 (2)$ K
$\gamma = 80.066 (2)°$	Columnar, pale yellow
$V = 3478.2 (4)$ Å³	$0.38 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART 6000 CCD area- detector diffractometer	23700 measured reflections 23700 independent reflections
ω scans	23095 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2002; Blessing, 1995)	$\theta_{max} = 27.9°$ $h = -13 \rightarrow 13$ $k = -17 \rightarrow 17$
$T_{min} = 0.62, T_{max} = 0.79$	$l = 0 \rightarrow 32$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 15.0158P]$
$wR(F^2) = 0.121$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.18$	$(\Delta/\sigma)_{max} = 0.003$
23700 reflections	$\Delta\rho_{max} = 2.01$ e Å⁻³
944 parameters	$\Delta\rho_{min} = -0.97$ e Å⁻³
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Tb1—O3	2.307 (3)	Tb2—O8	2.308 (4)
Tb1—O5	2.321 (3)	Tb2—O12	2.309 (4)
Tb1—O1	2.325 (3)	Tb2—O10	2.335 (4)
Tb1—O2	2.332 (3)	Tb2—O7	2.336 (3)
Tb1—O6	2.332 (3)	Tb2—O9	2.346 (3)
Tb1—O4	2.343 (3)	Tb2—O11	2.347 (4)
Tb1—N4	2.568 (4)	Tb2—N3	2.547 (4)
Tb1—N1	2.586 (4)	Tb2—N2	2.628 (4)
O1—Tb1—O2	73.30 (12)	O8—Tb2—O7	71.98 (12)
O5—Tb1—O6	73.40 (12)	O10—Tb2—O9	71.52 (12)
O3—Tb1—O4	72.42 (12)	O12—Tb2—O11	72.64 (13)
N4—Tb1—N1	63.12 (12)	N3—Tb2—N2	62.67 (12)

The refinement of the structure was complicated by twinning. The structure was identified as a non-merohedral twin using *RLATT* (Bruker, 1998). Two p4p files were written (*GEMINI*; Bruker, 2000) and combined into one twinp4p file that could be read by *SAINT* (Bruker, 2003). *SAINT* integrates with both orientation matrices and separates the twin components. Corrections for absorption and decay were applied using *TWINABS*. The twinning law is a 180° rotation about c^*. The final refinements were performed with all unique reflections using the HKLF 5 format in *SHELXTL* (Sheldrick, 2003). A partial structure solution was obtained by direct methods and the remaining non-H atoms were located using difference Fourier techniques. Two thiophene rings of the six tta ligands show positional disorder, which can be described as 180° rotations about the C—C bonds C27—C28 and C35—C36. The occupancies refined to 0.80:0.20 for the ring S3/C28–C31 and 0.50:0.50 for S4/C36–C39. Concomitantly, we find atoms of different elements (S and C) sharing almost the same site. SADI and EADP restraints were used to achieve a stable refinement for this disorder. Furthermore, four of the six tta CF_3 groups could be modeled as disordered groups. The refined model contained two or three positions for each of the F atoms with the following occupancies: F7/F8/F9 0.50:0.25:0.25; F10/F11/F12 0.55:0.45; F13/F14/F15 0.50:0.25:0.25; and F16/F17/F18 0.55:0.45. One SADI restraint was required for a stable refinement (C40—F10A and C40—F10B). Additionally, the ethyl acetate solvent molecule exhibits a 0.70:0.30 disorder of the terminal methyl group.

All non-disordered non-H atoms were refined with anisotropic atomic displacement parameters and disordered atoms were refined isotropically. The H atoms were calculated in idealized positions, with C—H = 0.95–0.99 Å, and included in the refinement as constrained atoms with appropriate occupancies, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2003); program used to solve structure: *SHELXS97* (Sheldrick, 1997); program used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2004).

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