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Hexakis(antipyrine-*O*)terbium(III) triperchlorate

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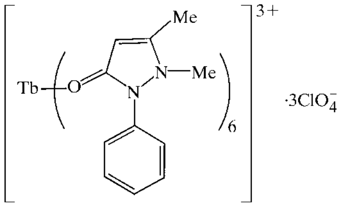
In the title compound, hexakis(1,2-dihydro-1,5-dimethyl-2-phenyl-3*H*-pyrazol-3-one-*O*)terbium(III) triperchlorate, $[Tb(C_{11}H_{12}N_2O)_6](ClO_4)_3$, the Tb atom lies on a site of $\overline{3}$ crystallographic symmetry and the unique Tb—O distance is 2.278 (2) Å. One of the perchlorate anions has threefold crystallographic symmetry, while the other is disordered about a $\overline{3}$ site.

Comment

As a bulky monodentate ligand with a hard O atom as donor, antipyrine has long been known to form complexes with transition and alkaline-earth metals, as well as rare-earth metals. Its lanthanide complexes have drawn much attention primarily due to the interest in exploring their luminescent properties. The lanthanide nitrates or iodides react steadily with antipyrine to offer complexes involving three or six antipyrines (Baker & Jeffery, 1974), in which a brilliantly triboluminescent characteristic was found (Rheingold & King, 1989). Our interests in finding highly luminescent terbium(III) or europium(III) complexes led us to synthesize a series of lanthanide complexes incorporating aromatic heterocyclic ligands (Su *et al.* 1997, 1998, 1999). This paper reports the structure of a terbium(III) antipyrine complexe with perchlorate as counter-anion, (I), which servers as a complement for comparison with the nitrate and iodide complexes.



(I)

The X-ray structure estabilshes that (I) consists of a discrete monomeric $[Tb(C_{11}H_{12}N_2O)_6]^{3+}$ cation and three perchlorate anions. The central terbium(III) ion is in an octahedral geometry, bonding to O atoms of six antipyrine ligands. The molecule possesses $\overline{3}$ symmetry, with the Tb atom residues at inversion centers. So the six antipyrines are S_6 related with only one unique, and the six Tb—O bonds are identical with a distance of 2.278 (2) Å. The O—Tb—O angles of 88.96 (8), 91.04 (8) and 180° closely resemble the theoretical values, indicating that the coordination polyhedral of the terbium(III) ion is normal as predicted by ligand-field theories. The benzene ring and pyrazole ring are both planar with mean-plane equations $12.491X - 0.860Y + 1.516Z = -3.4899$ and $1.745X + 11.099Y + 2.329Z = 0.0795$, and mean deviations of 0.0036 and 0.0133 Å, respectively.

One of the perchlorate anions possesses a threefold axis passing through one Cl—O bond, while another lies on a symmetry center with the O atoms S_6 disordered, each set of ClO_4^- anion possessing half occupancy.

Experimental

The title compound was obtained from the reaction of hydrated $Tb(ClO_4)_3$ with antipyrine in a 1:3 molar ratio in MeOH–MeCN mixed medium (*v*/*v* 1:1). Vapour diffusion of diethyl ether into the dilute reaction mixture gave colorless crystals suitable for single-crystal X-ray structure determination.

Crystal data

$[Tb(C_{11}H_{12}N_2O)_6](ClO_4)_3$
$M_r = 1586.63$
Trigonal, $R\overline{3}$
$a = 13.9691\ (10)$ Å
$c = 32.390\ (3)$ Å
$V = 5473.6\ (8)$ Å^3
$Z = 3$
$D_x = 1.444$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 980 reflections
$\theta = 2.6$–$16.8°$
$\mu = 1.154$ mm^{-1}
$T = 293\ (2)$ K
Block, colorless
$0.21 \times 0.15 \times 0.06$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.793$, $T_{\max} = 0.933$
12 276 measured reflections
2800 independent reflections

2688 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.054$
$\theta_{\max} = 27.52°$
$h = -9 \rightarrow 18$
$k = -18 \rightarrow 18$
$l = -42 \rightarrow 39$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.110$
$S = 1.042$
2800 reflections
160 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.017$
$\Delta\rho_{\max} = 0.80$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}

Difference maps indicated that the methyl H atoms at C4 and C5 were possibly disordered and these H atoms were allowed for at C4 and C5 by placing six 0.5-occupancy equally spaced riding H atoms at these sites.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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