

Hexakis(antipyrine-*O*)terbium(III) triiodide at 160 K: confirmation of a centrosymmetric structure for a brilliantly triboluminescent complex**William Clegg,^{a*} Grant Bourhill^{b†} and Ian Sage^b**^aDepartment of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England, and ^bSensors and Electronics Division, E-911, QinetiQ, Malvern WR14 3PS, England

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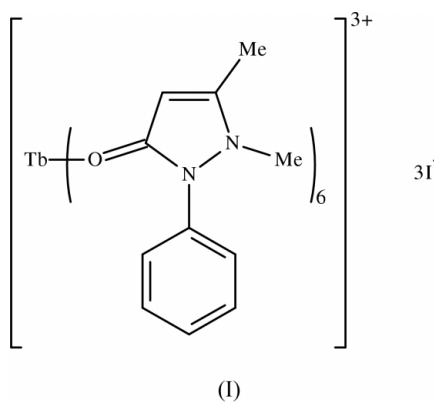
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Key indicatorsSingle-crystal X-ray study
T = 160 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.019
wR factor = 0.047
Data-to-parameter ratio = 21.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex, $[\text{Tb}(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_6]\text{I}_3$, has essentially the same structure at 160 K as at room temperature, and is clearly centrosymmetric without any disorder, contrary to some proposals regarding the possible mechanism of triboluminescence. Terbium has an octahedral coordination and lies in a position of $\bar{3}$ symmetry, with all six antipyrine ligands crystallographically equivalent. One iodide anion lies in a special position of site symmetry $\bar{3}$, and another is on a threefold rotation axis, to give three iodide anions per terbium-centred complex cation.

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Triboluminescence is the property whereby some crystalline solid materials emit light upon fracture. It has been known for centuries, and is exhibited by a wide range of materials including such common substances as sucrose. Many of the materials known to be triboluminescent display only weak emission on fracture, but there are some materials for which the effect is so strong that the emitted light can clearly be seen in broad daylight. Notable among these are numerous lanthanide complexes. These are of considerable current interest as potential damage sensors in composite and other materials (Sage & Bourhill, 2001; Sage *et al.*, 1999).



The mechanism (or mechanisms) of triboluminescence is poorly understood, and there is considerable debate over the requirement or otherwise for a non-centrosymmetric crystal structure in order for the phenomenon to be observed. Although numerous centrosymmetric structures have been reported, even for strongly triboluminescent materials (Sweeting & Rheingold, 1987; Rheingold & King, 1989; Chen *et al.*, 1998; Chen *et al.*, 1999; Chen *et al.*, 2000; Chen *et al.*, 2001), these have often included structural disorder, to which appeal has been made as a possible cause of triboluminescent

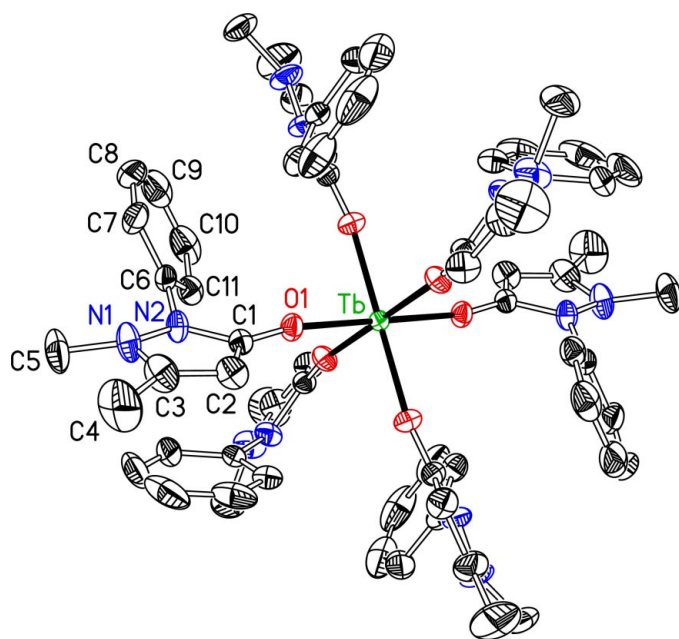


Figure 1
The cation structure of (I) with atom labels and 50% probability ellipsoids for non-H atoms.

activity, though without any convincing explanation of how this could operate. In the case of one particular europium complex, an initial report of a disordered centrosymmetric structure (space group $I2/a$; Sweeting & Rheingold, 1987) has more recently been refuted, with a correction to a non-centrosymmetric structure (space group Ia) with a lower degree of disorder (Cotton *et al.*, 2001). These authors imply that similar revisions may be necessary for other complexes.

The title complex, (I), is brilliantly triboluminescent. Its crystal structure, determined at room temperature, was reported by Rheingold & King (1989), following an earlier study by Van Uitert & Soden (1962). The space group, $R\bar{3}$, is one that can not be distinguished from a non-centrosymmetric group, $R3$, on the basis of systematic absences, and statistical tests on the distribution of intensities are unreliable in the presence of a very heavy atom such as terbium. There were, however, no indications of disorder or other features suggestive of a possible incorrect space-group assignment.

As part of a study of triboluminescent lanthanide complexes with potential application as structural damage sensors, including the variation of structure with conditions, we have redetermined the structure of the title complex at reduced temperature. The results are of markedly greater precision, and they show negligible residual electron density, unexceptional atomic displacements, and a total absence of any indication of disorder (Fig. 1); we have a very high level of confidence in the assignment of the centrosymmetric space group, and the material appears to be of high purity. The origin of the brilliant triboluminescence does not lie in non-centrosymmetry or in structural disorder, and the phenomenon must be explained in some other way. Further research is in progress to investigate this.

The complex cation has all six ligands equivalent by symmetry, the Tb ion lying in a special position of site symmetry $\bar{3}$, with essentially ideal octahedral coordination geometry (Table 1). There are two crystallographically independent iodide anions: one has site symmetry $\bar{3}$, and the other lies on a threefold rotation axis.

A search of the Cambridge Structural Database (Allen & Kennard, 1993) provides information on over thirty structures containing antipyrine as a ligand or other component. These include numerous co-crystals of antipyrine with lanthanide nitrates as well as other metal salts and complexes. The triperchlorate salt analogous to the title complex is isomorphous, with disorder in the anions and in the methyl groups of antipyrine (Su *et al.*, 2000), and the yttrium complex with iodide anions is fully isostructural (Baker & Jeffery, 1974).

Experimental

The title complex was prepared by a method described previously (Soden, 1961; Wilke-Dörfurt & Schliephake, 1928).

Crystal data

$[\text{Tb}(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_6]\text{I}_3$
 $M_r = 1668.98$
 Rhombohedral (on hexagonal axes), $R\bar{3}$
 $a = 13.7474(3) \text{ \AA}$
 $c = 31.9658(14) \text{ \AA}$
 $V = 5231.9(3) \text{ \AA}^3$
 $Z = 3$
 $D_x = 1.589 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 12573 reflections
 $\theta = 3.0\text{--}28.9^\circ$
 $\mu = 2.40 \text{ mm}^{-1}$
 $T = 160(2) \text{ K}$
 Block, colourless
 $0.50 \times 0.40 \times 0.35 \text{ mm}$

Data collection

Bruker SMART 1K CCD diffractometer
 ω rotation with narrow frames
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997a)
 $T_{\text{min}} = 0.387$, $T_{\text{max}} = 0.492$
 15672 measured reflections

2945 independent reflections
 2692 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 28.9^\circ$
 $h = -17 \rightarrow 17$
 $k = -18 \rightarrow 18$
 $l = -43 \rightarrow 43$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.019$
 $wR(F^2) = 0.047$
 $S = 1.10$
 2945 reflections
 137 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2 + 8.1659P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.00009(3)

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|-------------------------|-------------|----------|-------------|
| Tb—O1 | 2.2367 (11) | N2—C1 | 1.381 (2) |
| O1—C1 | 1.261 (2) | C1—C2 | 1.406 (2) |
| N1—N2 | 1.385 (2) | C2—C3 | 1.370 (3) |
| N1—C3 | 1.347 (3) | | |
| O1—Tb—O1 ⁱ | 87.75 (4) | O1—C1—N2 | 120.96 (15) |
| O1—Tb—O1 ⁱⁱ | 92.25 (4) | O1—C1—C2 | 132.34 (17) |
| O1—Tb—O1 ⁱⁱⁱ | 180.0 | N2—C1—C2 | 106.65 (15) |
| Tb—O1—C1 | 170.00 (12) | C1—C2—C3 | 107.11 (18) |
| N2—N1—C3 | 107.60 (15) | N1—C3—C2 | 109.97 (17) |
| N1—N2—C1 | 108.47 (14) | | |

Symmetry codes: (i) $-x + y, -x, z$; (ii) $y, -x + y, -z$; (iii) $-x, -y, -z$.

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with U_{iso}

constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997b); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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