

## Two isostructural triboluminescent lanthanide complexes

William Clegg,<sup>a\*</sup> Ian Sage,<sup>b</sup> Iain Oswald,<sup>b</sup> Peter Brough<sup>c</sup>  
and Grant Bourhill<sup>b†</sup>

<sup>a</sup>Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England, <sup>b</sup>Sensors and Electronics Sector, DERA, St Andrews Road, Great Malvern WR14 3PS, England, and <sup>c</sup>DERA Fort Halstead, Weapons Sector, Sevenoaks, Kent TN14 7BP, England  
Correspondence e-mail: w.clegg@ncl.ac.uk

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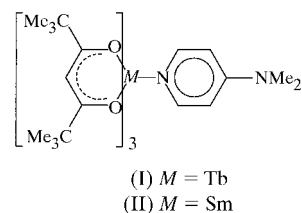
(4-Dimethylaminopyridine)tris(2,2,6,6-tetramethylheptane-3,5-dionato)terbium(III), [Tb(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>)<sub>3</sub>(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)], and its samarium analogue, [Sm(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>)<sub>3</sub>(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)], are isostructural. Their polar space group is consistent with observed second harmonic generation and with the involvement of piezoelectric charging in their intense triboluminescence properties, which are of interest for the development of damage sensors in composite materials. The metals display irregular seven-coordination by one substituted pyridine and three chelating diketonate ligands, bond lengths to Tb being shorter than those to Sm.

### Comment

Polymer composite materials are being used increasingly in commercial and military structures and equipment to replace metals because of their lower density and greater stiffness and strength. It is essential to monitor and locate damage in such materials resulting from accidental impact and other causes. Current methods are time consuming and costly since composites can often be severely damaged internally with little or no visual indication on the surface (Matthews, 1999). We have recently proposed the use of triboluminescent materials as smart structural damage sensors, which can indicate the incidence, severity and location of impact (Sage *et al.*, 1999; Sage & Geddes, 1999). Triboluminescent compounds emit light when fractured (Walton, 1977) and are thus ideal candidates for this purpose. The use of a number of different triboluminescent compounds, positioned at different locations on a structure, can enable a damage site to be identified by monitoring the wavelength of the light emission. This idea has been validated by preliminary proof-of-concept experiments (Sage, Badcock, Humberstone, Geddes, Kemp, Bishop & Bourhill, 1999; Sage, Badcock, Humberstone, Geddes, Kemp & Bourhill, 1999).

† Contact e-mail: gbourhill@dera.gov.uk.

The title compounds, namely (4-dimethylaminopyridine)-tris(2,2,6,6-tetramethylheptane-3,5-dionato)terbium(III), (I), and its samarium analogue, (II), are typical of triboluminescent materials we are currently investigating in this context. They have a number of properties suited to the application. It is particularly important that the triboluminescence is relatively intense. Most triboluminescence is difficult to observe, but a significant number of highly efficient triboluminescent materials have been reported (Goodgame & Cotton, 1961; Zink, 1975; Hurt & McAvoy, 1966). A high proportion contain lanthanide metals as the emitting centre (Hurt & McAvoy, 1966; Rheingold & King, 1989). These complexes generally exhibit extremely narrow and characteristic emission bandwidths, as well as high intensity, which makes them attractive as potential damage sensors. In many cases, they are also chemically stable under the conditions of composite material fabrication, so that they can be incorporated into the structural materials of interest.



One explanation often invoked for the phenomenon of triboluminescence is that of a stress-induced piezoelectric charging, leading to excitation of nitrogen gas molecules, followed by lanthanide excitation *via* direct energy transfer or an emission and reabsorption process (Walton, 1977; Takada, 1997). Such a mechanism requires a non-centrosymmetric crystal structure for the piezoelectric effect (Nye, 1989), assuming that the process of fracture itself does not distort a normally centrosymmetric structure into a non-centrosymmetric one (Chapman & Walton, 1983; Hocking *et al.*, 1989).

Compound (I) has been found to be compatible with embedding within high performance polymer composites, in addition to its desirable triboluminescent properties. The corresponding samarium complex, (II), has also been synthesized, to assess the feasibility of using the different emission wavelength for damage location monitoring. The crystal structures of (I) and (II) have been determined as the first stage of a proposed systematic programme investigating the relationship between triboluminescence and structure.

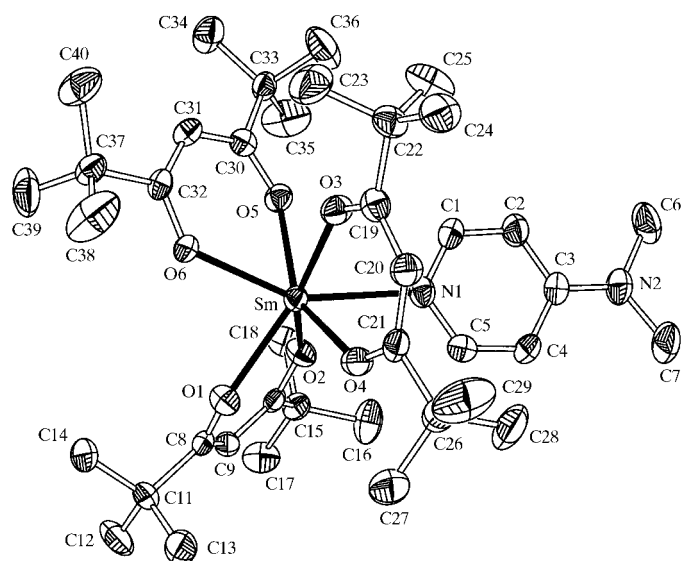
Both complexes are found to be highly triboluminescent. Solid-state triboluminescence and photoluminescence emission spectra have been measured with an optical multichannel analyser (Princeton Instruments ST130) at 1.75 nm resolution (Duignan *et al.*, 2000). We find that they arise from Tb<sup>III</sup> and Sm<sup>III</sup> oxidation states, as expected, and that the two spectra are essentially identical for each complex. This is consistent with the results from other lanthanide-containing triboluminescent compounds (Walton, 1977; Sweeting & Guido, 1985; Chen, 1999), showing that the light emission is from the same excited level regardless of whether the excitation is by fracture or by incident photons. The peak  $f-f$  transition wave-

length for compound (I) is 548 nm, and for compound (II) 648 nm (Duignan *et al.*, 2000). Positive second harmonic generation signals (Bourhill *et al.*, 1993) indicate that both compounds adopt non-centrosymmetric crystal structures.

The two compounds are found to be isostructural, crystallizing in the polar space group  $P2_1$ , consistent with the observed second harmonic generation properties. The structures consist of discrete neutral molecules (Fig. 1) in which the lanthanide is coordinated by three chelating diketonate ligands and by the substituted pyridine. Bond lengths to Tb are somewhat shorter than the corresponding values for Sm, as expected from the commonly observed lanthanide contraction effect (Tables 1 and 2). The metal atoms are in irregular seven-coordinate geometries in which four O atoms (O3 and O4 within the same ligand, and O2 and O5 from the other two ligands) lie approximately in a plane, with the remaining two O atoms (O1 and O6) below the plane and the N1 atom above it; the metal atom is displaced from the O<sub>4</sub> plane towards the other two O atoms by approximately 0.45 Å. Among other possible descriptions of the geometry, the coordination may thus be thought of as derived from octahedral, with one site replaced by two coordinating atoms. The necessarily narrow bite angle of the chelate ligands, around 72°, contributes to the irregularity of the geometry. The internal geometry of the ligands is unexceptional and there are no significant intermolecular interactions. There is no disorder in the structures; disorder has been suggested as a contributory factor in some cases of triboluminescence (Sweeting & Rheingold, 1987; Zeng *et al.*, 2000).

There are no notable intermolecular interactions. Although the dimethylamino N atom has the potential to form bridges between metal centres, the closest approach of N2 to the Tb or Sm atoms is more than 5.4 Å.

A search of the Cambridge Structural Database (April 2000 release; Allen & Kennard, 1993) shows that there are around



**Figure 1**  
The molecular structure of (II) with atom labels and 50% probability ellipsoids for non-H atoms; H atoms have been omitted. The corresponding view of (I) is very similar.

100 known structures of lanthanide complexes with three chelating  $\beta$ -diketonate ligands, in addition to about 40 neutral or anionic complexes having four such ligands. High coordination numbers for lanthanides are common, and most of these structures with three  $\beta$ -diketonate ligands also have at least one other bidentate or two monodentate ligands. For most of the complexes with just one monodentate ligand, this is a coordinated water molecule, with other oxygen donors also being well represented. In the case of neutral substituted or unsubstituted pyridine ligands, there may be one (Wasson *et al.*, 1973, and the current work) or two of these (Cramer & Seff, 1972; Horrocks *et al.*, 1971), or one with a coordinated water molecule also (Leipoldt *et al.*, 1976). For the small number of these complexes so far reported, there is thus no clear pattern in the qualitative coordination behaviour, and the coordination geometry of seven-coordinate lanthanide complexes with three  $\beta$ -diketonate ligands appears to be quite flexible. The isostructural nature of the two complexes reported here suggests that the substituents on the ligands may play a dominant role in the angular coordination geometry, with the choice of lanthanide affecting the bond lengths around it.

The results of this study are consistent with the proposed piezoelectric mechanism for triboluminescence of these materials, though this does not constitute proof of the mechanism. The fact that the two complexes are isostructural, while displaying markedly different emission spectra, supports our suggestion that a series of related lanthanide complexes with different metals may be used as location-sensitive damage sensors. This work provides a foundation and encouragement for further research in the area.

## Experimental

For the preparation of compound (I), 4-(dimethylamino)pyridine (12.14 g, 99.4 mmol) dissolved in dry ethanol (100 ml) was added slowly to a solution of tris(2,2,6,6-tetramethylheptane-3,5-dionato)-terbium(III) (70 g, 98.8 mmol) in dry ethanol (1000 ml), giving a cloudy grey solution. This solution was heated gently at 333 K for 2.5 h and the clear grey solution was allowed to cool to room temperature. Filtration through silica gel gave a very pale yellow solution, from which a pale yellow precipitate was obtained after concentration. The solid was dried *in vacuo* and recrystallized from hot acetonitrile to give the desired product in 95% yield; m.p. 422–423 K. Analysis, calculated: C 57.8, H 8.1, N 3.4, Tb 19.1%; found: C 57.3, H 8.1, N 3.3, Tb 19.5%. For the preparation of compound (II), the same procedure was used with the corresponding samarium complex (70 g, 100 mmol); 95% yield, m.p. 414–416 K.

## Compound (I)

### Crystal data

[Tb(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>)<sub>3</sub>(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)]  
 $M_r = 830.88$   
 Monoclinic,  $P2_1$   
 $a = 10.9465$  (11) Å  
 $b = 18.972$  (2) Å  
 $c = 11.0469$  (12) Å  
 $\beta = 110.643$  (2)°  
 $V = 2146.9$  (4) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.285$  Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 Cell parameters from 5819 reflections  
 $\theta = 2.50$ – $28.62^\circ$   
 $\mu = 1.690$  mm<sup>-1</sup>  
 $T = 160$  (2) K  
 Prism, colourless  
 0.40 × 0.25 × 0.18 mm

**Table 1**

Selected geometric parameters (Å, °) for (I).

Tb—O6	2.282 (2)	Tb—O4	2.313 (2)
Tb—O3	2.296 (2)	Tb—O5	2.320 (2)
Tb—O2	2.298 (2)	Tb—N1	2.527 (3)
Tb—O1	2.3006 (18)		
O2—Tb—O1	72.12 (12)	O2—Tb—N1	73.83 (8)
O3—Tb—O4	73.55 (8)	O1—Tb—N1	127.16 (9)
O6—Tb—O5	73.32 (7)	O4—Tb—N1	78.34 (8)
O6—Tb—N1	154.26 (8)	O5—Tb—N1	85.63 (8)
O3—Tb—N1	81.36 (8)		

*Data collection*

Siemens SMART CCD diffractometer  
 $\omega$  rotation with narrow frames  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)  
 $T_{\min} = 0.551$ ,  $T_{\max} = 0.751$   
 18 460 measured reflections

9868 independent reflections  
 9418 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$   
 $\theta_{\text{max}} = 28.67^\circ$   
 $h = -14 \rightarrow 14$   
 $k = -24 \rightarrow 25$   
 $l = -14 \rightarrow 14$

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.054$   
 $S = 1.186$   
 9868 reflections  
 463 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0140P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.24 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -2.54 \text{ e } \text{Å}^{-3}$  (2.4 Å from Tb)  
 Extinction correction: SHELXTL  
 Extinction coefficient:  
 $6.2 (18) \times 10^{-4}$   
 Absolute structure: Flack (1983);  
 4588 Friedel pairs  
 Flack parameter = 0.019 (7)

**Compound (II)**

*Crystal data*

[Sm(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>)<sub>3</sub>(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)]  
 $M_r = 822.31$   
 Monoclinic,  $P2_1$   
 $a = 10.9846 (5) \text{ Å}$   
 $b = 18.9758 (8) \text{ Å}$   
 $c = 11.0865 (5) \text{ Å}$   
 $\beta = 110.833 (2)^\circ$   
 $V = 2159.80 (17) \text{ Å}^3$   
 $Z = 2$

$D_x = 1.264 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 4928 reflections  
 $\theta = 2.24\text{--}27.78^\circ$   
 $\mu = 1.402 \text{ mm}^{-1}$   
 $T = 160 (2) \text{ K}$   
 Prism, colourless  
 $0.50 \times 0.50 \times 0.25 \text{ mm}$

*Data collection*

Siemens SMART CCD diffractometer  
 $\omega$  rotation with narrow frames  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)  
 $T_{\min} = 0.578$ ,  $T_{\max} = 0.704$   
 13 396 measured reflections

7953 independent reflections  
 6733 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$   
 $\theta_{\text{max}} = 28.84^\circ$   
 $h = -14 \rightarrow 12$   
 $k = -13 \rightarrow 25$   
 $l = -14 \rightarrow 15$

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.047$   
 $S = 0.938$   
 7953 reflections  
 463 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0202P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.003$   
 $\Delta\rho_{\text{max}} = 0.65 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.49 \text{ e } \text{Å}^{-3}$   
 Extinction correction: SHELXTL  
 Extinction coefficient:  
 $91 (13) \times 10^{-4}$   
 Absolute structure: Flack (1983);  
 2642 Friedel pairs  
 Flack parameter = 0.007 (7)

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds; C—H = 0.95–0.98 Å) and with  $U_{\text{iso}}$  constrained to be 1.2 (1.5 for methyl groups) times  $U_{\text{eq}}$  of the carrier atom.

**Table 2**

Selected geometric parameters (Å, °) for (II).

Sm—O6	2.326 (2)	Sm—O4	2.354 (2)
Sm—O1	2.3323 (19)	Sm—O5	2.364 (2)
Sm—O3	2.333 (2)	Sm—N1	2.578 (3)
Sm—O2	2.341 (2)		
O1—Sm—O2	71.06 (13)	O3—Sm—N1	81.42 (9)
O3—Sm—O4	72.26 (8)	O2—Sm—N1	73.60 (8)
O6—Sm—O5	71.87 (7)	O4—Sm—N1	78.16 (8)
O6—Sm—N1	153.57 (8)	O5—Sm—N1	86.04 (8)
O1—Sm—N1	126.90 (9)		

For both compounds, data collection: SMART (Siemens, 1995); cell refinement and data reduction: SAINT (Siemens, 1995); program(s) used to solve and refine structure: SHELXTL (Sheldrick, 1994); molecular graphics: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1415). Services for accessing these data are described at the back of the journal.

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