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Triboluminescence and crystal structures of non-ionic europium complexes

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The triboluminescence of three non-ionic europium complexes, Eu(TTA)$_3$·bipy (**1**), Eu(TTA)$_3$·dia (**2**) and Eu(DBM)$_3$·dmbp·H$_2$O (**3**) (TTA = 2-thenoyltrifluoroacetonate, DBM = dibenzoylmethanate, bipy = 2,2′-bipyridine, dia = 4,5-diazafluoren-9-one, dmbp = 4,4′-dimethyl-2,2′-bipyridinate), was observed. Structure determinations of **1** and **3** were carried out. The triboluminescence maxima of **1** and **2** are similar to those of their photoluminescence. The disorder of the thienyl ring and CF$_3$ groups in **1** and the disorder of water in the packing of **3** may be responsible for their triboluminescent activity.

Introduction

When some solids are subject to stress beyond a certain level, emission of light occurs. This mechanically induced luminescence is known as triboluminescence. Although triboluminescence is a well known phenomenon, its mechanism can not be completely accounted for and hence no predictions can be made concerning the occurrence of particularly intense triboluminescent compounds. In recent years, complexes of the lanthanide elements exhibiting brilliant triboluminescent properties have received much attention since these complexes can be used for optical sensors, being sensitive to impact, tension or pressure.[1] On the other hand, for the construction of a predictive theory of triboluminescence, extensive searches for a clear pattern of triboluminescent activity as a function of crystal structure have been made.[2] Over the years, the strong correlation of non-centrosymmetric crystal structure with triboluminescence has led most observers to conclude that the piezoelectric properties of non-centrosymmetric crystals are always the source of triboluminescence. However, many centrosymmetric crystals which are triboluminescent are known, as are many non-centrosymmetric crystals which are not.[3] Sweeting *et al.* believe that a non-centrosymmetric crystal structure is necessary for tribophotoluminescence in pure covalent compounds[2f] and that impurities or disorders may play important roles in the triboluminescent activity of centrosymmetric materials.[2a] We recently found that disordered S and F atoms in centrosymmetric 1,4-dimethylpyridinium tetrakis(2-thenoyltrifluoroacetonato)europate(III) may be responsible for its triboluminescent activity.[4] In this paper, we report the triboluminescent activities of non-ionic complexes **1**, **2** and **3**, the triboluminescence spectra of **1** and **2** and the crystal structures of **1** and **3**. Although the preparation of **1** and **2** has been reported previously,[5] their triboluminescent activity and crystal structures have, to the best of our knowledge, not yet been reported.

Experimental

Synthesis

All the chemicals were of analytical grade and were used without further purification. 4,5-Diazafluoren-9-one was synthesized according to the literature method.[6]

Complexes **1** and **2** were prepared according to the literature methods.[5] Complex **3** was prepared as follows. A solution of 1 mmol EuCl$_3$ in 10 ml EtOH was added dropwise to a hot solution of 3 mmol dibenzoylmethane and 1 mmol 4,4′-dimethyl-2,2′-bipyridine in 10 ml EtOH and the resultant mixture was kept under air. After a few days, pale yellow products were obtained. Purification was accomplished by recrystallization. Single crystals suitable for X-ray crystallography were obtained from Me$_2$CO–EtOH for **1** and from MeCN–EtOH for **3**. The analytical data are shown in Table 1.

Physical measurements

Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. Triboluminescence spectra were obtained using an Acton Research Corporation (ARC) SpectraPro-750, Santa Barbara Instruments Group (SBIG) CCD Detection System. The grating chosen was blazed for 500 nm with 1200 grooves per mm. The 10 μm slit used gave a resolution of 0.023 nm. Wavelength accuracy was ± 0.1 nm with the 1200 groove mm^{-1} grating. A calibration curve was acquired from an uncrushed sample with no triboluminescence and was set as the background. The calibration curve was subtracted from each new curve input from the camera. The sample was placed as close as possible to the slit in the quartz colorimetric tube and was ground by hand, drawing up a small portion with a glass rod and crushing it against the side of the tube. Photoluminescence spectra were obtained with an ARC SpectraPro-750, (SBIG) CCD instrument and an Nd : YAG laser. The 355 nm laser line of Nd : YAG with a 20 ns pulse width was used to pump the sample.

X-Ray crystallography

X-Ray crystallography was performed using a Siemens SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Crystal data are listed in Table 2. The data were corrected for Lorentz and polarization effects during data reduction using SADABS.[7] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL Version 5.03[8] for **1** and SHELXTL-97[9] for **3**. All non-hydrogen atoms were refined anisotropically. In complex **1**, the terminal CF$_3$

Table 1 Analytical data for complexes **1–3**

Compound	Formula	mp/°C	Analysis: Found (Calc.) %C	%H	%N
Eu(TTA)$_3$·bipy (**1**)	Eu(C$_8$H$_4$O$_2$F$_3$S)$_3$·C$_{10}$H$_8$N$_2$	220–222	41.80 (42.02)	1.96 (2.06)	2.71 (2.88)
Eu(TTA)$_3$·dia (**2**)	Eu(C$_8$H$_4$O$_2$F$_3$S)$_3$·C$_{11}$H$_6$N$_2$O	230–232	42.22 (42.13)	1.82 (1.81)	2.60 (2.81)
Eu(DBM)$_3$·dmbp·H$_2$O (**3**)	Eu(C$_{15}$H$_{11}$O$_2$)$_3$·C$_{12}$H$_{12}$N$_2$·H$_2$O	166–168	67.11 (66.90)	4.65 (4.59)	2.91 (2.73)

groups are disordered due to free rotation about the C–C bonds. The S(3) atoms and the *ortho*-carbon C(29) atoms were also found to be disordered. The occupancies of the S(3) and C(29) atoms were refined to 0.677 and 0.322, respectively. All computations were carried out using the SHELXTL Version 5.03 package.[8] Selected bond lengths and bond angles are listed in Table 3.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/177. See http://www.rsc.org/suppdata/jm/1999/2919 for crystallographic files in .cif format.

Results and discussion

Description of the structures

ORTEP drawings of **1** and **3** are shown in Fig. 1 and 2, respectively. We were unable to grow single crystals of **2** suitable for crystallographic analysis, although its structure may be similar to those of **1** and **3**. The complexes **1** and **3** crystallize in the monoclinic space group ($P2_1/n$) with four molecules in the unit cell. However, there is only one molecule per asymmetric unit for complexes **1** and **3**. As expected, **1** and **3** are both tetra-bidentate, eight-coordinate Eu(III) complexes each containing three β-diketonate chelates and one *N*,*N*′-bidentate ligand. The coordination geometry of both the Eu(III) centres is best described as a square antiprism. For **1**, the two square planes are [O(1)O(2)N(1)N(2)] (with a deviation of 0.0458 Å) and [O(3)O(4)O(5)O(6)] (with a deviation of 0.0124 Å). The dihedral angle between [O(1)O(2)N(1)N(2)] and [O(3)O(4)O(5)O(6)] is 2.6°. The square planes are [O(1)O(2)O(3)O(4)] (with a deviation of 0.057 Å) and [O(5)O(6)N(1)N(2)] (with a deviation of 0.0895 Å) for **3**. The dihedral angle between [O(1)O(2)O(3)O(4)] and [O(5)O(6)N(1)N(2)] is 2.9°. The average Eu–O bond lengths in **1** (2.3517 Å) and **3** (2.3508 Å) are somewhat shorter than for Eu(btfa)$_3$·bipy (2.360 Å) (btfa = 4,4,4-trifluoro-1-phenyl-1,3-butanedione).[10] The average Eu–N distance in **1** (2.5775 Å) is shorter than in **3** (2.6005 Å). The O–Eu–O angles within the chelate rings have the same average value of 72.13° for both **1** and **3**. The CF$_3$ groups are commonly disordered in substituted β-diketonate complexes, and such is the case in complex **1**. Only one of the three thienyl rings in complex **1** shows disorder. Unlike **1**, the packing of complex **3** contains a water molecule

Table 3 Selected bond distances (Å) and angles (°) for **1** and **3**

	1	**3**
Eu–O(1)	2.343(5)	2.349(4)
Eu–O(2)	2.362(5)	2.332(4)
Eu–O(3)	2.362(5)	2.371(4)
Eu–O(4)	2.333(5)	2.326(4)
Eu–O(5)	2.353(5)	2.359(4)
Eu–O(6)	2.357(5)	2.368(4)
Eu–N(1)	2.558(6)	2.601(5)
Eu–N(2)	2.597(6)	2.600(4)
O(1)–Eu–O(2)	71.9(2)	71.97(13)
O(3)–Eu–O(4)	73.0(2)	72.90(13)
O(5)–Eu–O(6)	71.5(2)	71.52(13)
N(1)–Eu–N(2)	62.1(2)	61.16(15)

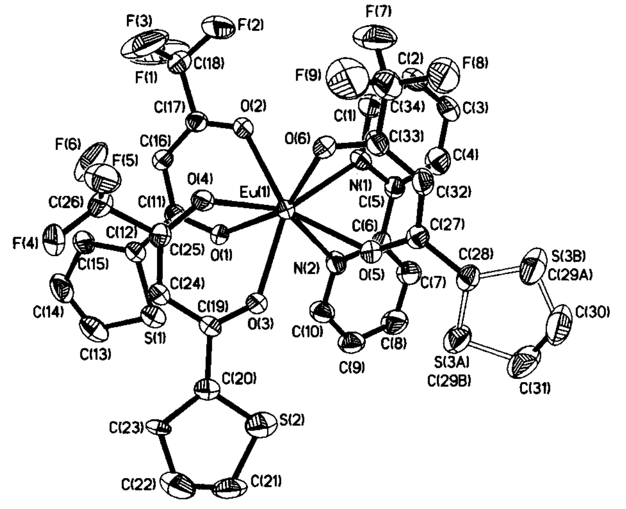

Fig. 1 The molecular structure of complex **1** (all hydrogen atoms are omitted for clarity).

Table 2 Crystallographic data for **1** and **3**

Complex	**1**	**3**
Formula	Eu(C$_8$H$_4$O$_2$F$_3$S)$_3$·C$_{10}$H$_8$N$_2$	Eu(C$_{15}$H$_{11}$O$_2$)$_3$·C$_{12}$H$_{12}$N$_2$·H$_2$O
Formula weight	971.66	1023.93
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	10.3148(2)	12.2720(2)
b/Å	16.8937(4)	23.5505(4)
c/Å	21.7803(3)	16.8123(3)
β/°	103.515(3)	99.8180(10)
V/Å^3	3690.23(12)	4787.79(14)
Z	4	4
μ/mm^{-1}	1.962	1.366
Reflections	23687	30863
Unique reflections	8449 ($R_{int} = 0.0730$)	10960 ($R_{int} = 0.1017$)
R,*wR* [$I > 2\sigma(I)$]	0.0630, 0.1348	0.0671, 0.0866

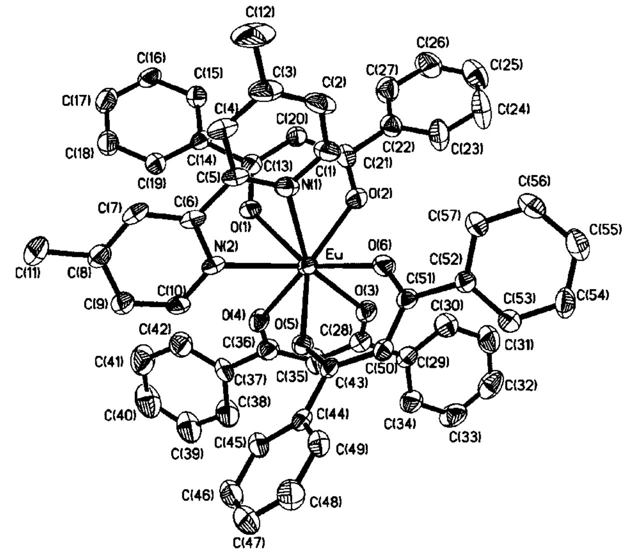

Fig. 2 The molecular structure of complex **3** (all hydrogen atoms are omitted for clarity).

for which disorder is indicated by the large value of its displacement parameter [$U_{eq}=289(7)$ Å^2.

Photoluminescence

The complexes **1–3** are very strongly luminescent, emitting red light when excited with 355 nm laser radiation. The solid-state photoluminescence emission spectra of **1–3** are shown in Fig. 3(a), Fig. 4(a) and Fig. 5, respectively. These emissions are typical of europium centered transitions from $^5D_0$ levels to the lower $^7F_{0-4}$ levels of the ground-state multiplet. The main emissions occur, as expected, in the $^5D_0 \rightarrow {}^7F_2$ transition. The presence of $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ transitions points to the Eu(III) ion having a structural environment of low symmetry. From the structural analysis, the site symmetries of **1** and **3** were assigned as C_s or C_2.[11] Moreover, the $^5D_0 \rightarrow {}^7F_0$ transition is a singlet, which indicates the presence of only a singlet emitting species. This is in agreement with the observation that there is only one molecule per asymmetric unit for complexes **1** and **3**, respectively.

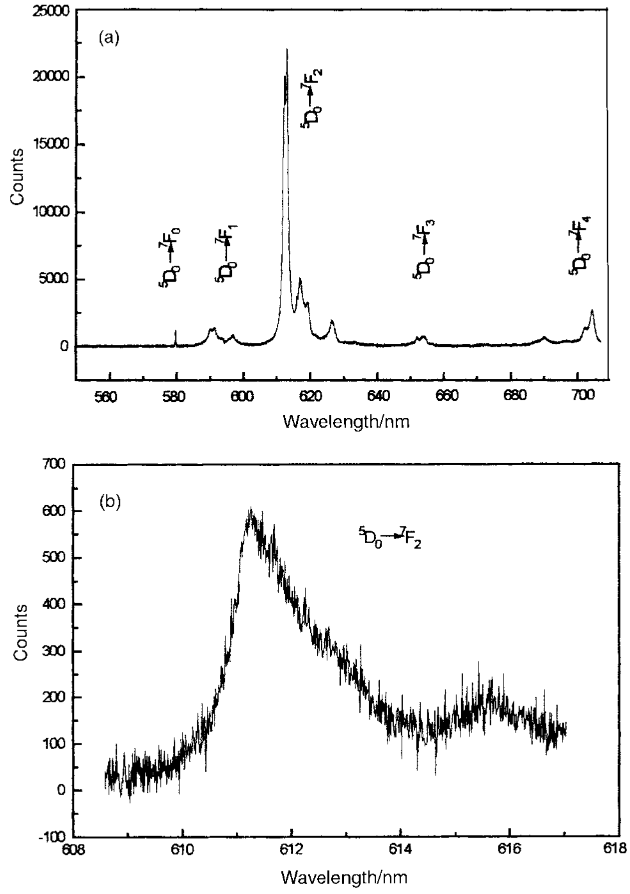

Fig. 3 (*a*) Emission spectrum ($\lambda_{ex}=355$ nm) of solid **1** at room temperature. (*b*) Triboluminescence spectrum of **1** at room temperature.

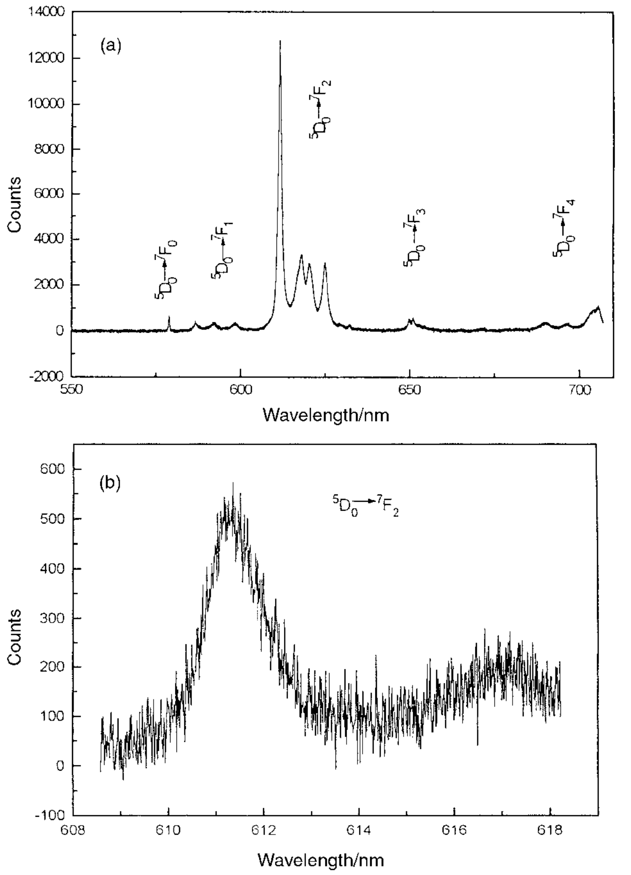

Fig. 4 (*a*) Emission spectrum ($\lambda_{ex}=355$ nm) of solid **2** at room temperature. (*b*) Triboluminescence spectrum of **2** at room temperature.

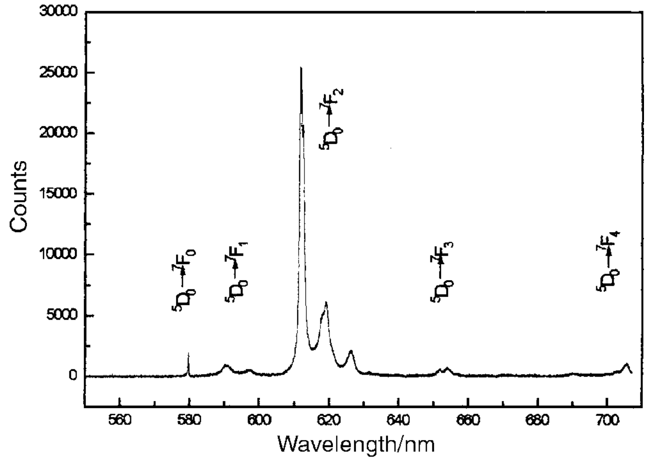

Fig. 5 Emission spectrum ($\lambda_{ex}=355$ nm) of solid **3** at room temperature.

Triboluminescence

The triboluminescent activities of **1–3** were tested upon initial crystallization. Crude samples of **1** and **3** exhibit red triboluminescence in darkness, whilst crude **2** exhibits red triboluminescence in daylight. After recrystallization from different solvents such as MeOH, EtOH, MeCN or Me_2CO, we note that the triboluminescent intensities of **1** and **3** were strengthened. They emit red triboluminescence in daylight. But **2** exhibits no obvious change in triboluminescence after recrystallization. The triboluminescent intensities of **1–3** decreased upon grinding in air. The triboluminescence spectra of **1** and **2** are shown in Fig. 3(b) and 4(b), respectively. The maxima in the triboluminescence spectra of **1** and **2** are essentially at the same wavelengths as those in the photoluminescence spectra. There are no detectable dinitrogen emissions. The triboluminescence emissions are weaker than those due to photoluminescence so only those parts of the triboluminescence emissions corresponding to the most intense photoluminescence emissions were observed. Rheingold and King stated that the most visible component of the triboluminescent emission of lanthanide complexes is the characteristic photoluminescence of the metallic elements.[2c] Therefore, the triboluminescence is assigned to the same excited state as the photoluminescence.

There is considerable evidence that triboluminescence is an electrical phenomenon, with charge separation the primary event. The recombination of charges separated during fracture results in triboluminescence. So triboluminescent activity is usually assumed to be a consequence of crystal asymmetry, *i.e.* only piezoelectric (non-centrosymmetric) crystals may be triboluminescent since only such crystals can develop opposite charges on the opposing faces of a developing crack. However, the multitude of reports of centrosymmetric triboluminescent materials casts doubt on that assumption. The present study again demonstrates that centrosymmetric materials can be triboluminescent. Rheingold and King suggest that ionic compounds may permit charge separation by partial fracture along planes with opposite charges.[2c] The complexes **1–3** are non-ionic compounds, they could not obtain the local piezoelectricity essential to their triboluminescent activities in weak interionic interactions capable of deformation on application of pressure. The importance of trace dopants in determining triboluminescent activity was proven for saccharin.[2d] Since the complexes **1**, **2** and **3**, recrystallized from the crude products, still exhibit triboluminescence, impurities seem not to be responsible for their triboluminescence. In their discussion of the relation between the structure and triboluminescent activity of triethylammonium tetrakis(dibenzoylmethanato)europate, Sweeting and Rheingold thought that the disorder of phenyl rings and cation may provide a sufficient source of localized polarity to produce the observed activity.[2a] We are now faced with a similar example, and a similar effect is also evident in **1**. The complex **1** is centrosymmetric and there is disorder of one thienyl ring and three CF_3 groups. This disorder may provide a structural basis for charge separation by creating randomly distributed sites of slightly different ionization potentials and electron affinities at the faces of developing cracks. Therefore, we think that the disorder of the thienyl ring and CF_3 groups may play an important role in the triboluminescence of centrosymmetric **1**. In contrast to **1,** the packing of centrosymmetric **3** contains a water molecule and is very stable in air. **3** offers no obvious structural basis for triboluminescent activity except disorder of the water molecule. We failed to obtain crystals of **3** without water. But we found that **3** recrystallized from different solvents such as MeOH, EtOH, MeCN and Me_2CO still exhibits triboluminescence. No other factor can account for the unexpected triboluminescent activity of complex **3**. It is possible that disorder of the water molecule in the crystal packing provides the local asymmetry essential to support charge separation. Further research on this question is in progress.

Conclusions

Triboluminescent europates are hardly news, but with each successive complex studied we get a little closer to an understanding of the phenomenon. In this paper the triboluminescence of three non-ionic europium complexes **1**, **2** and **3** was studied. The triboluminescence maxima of **1** and **2** are similar to those in their photoluminescence spectra, indicating identical emitting species. The crystal structures of **1** and **3** are centrosymmetric and disorder of a thienyl ring and the CF_3 groups in **1** and the disordered water molecule in the crystal packing of **3** may be responsible for their triboluminescent activities.

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