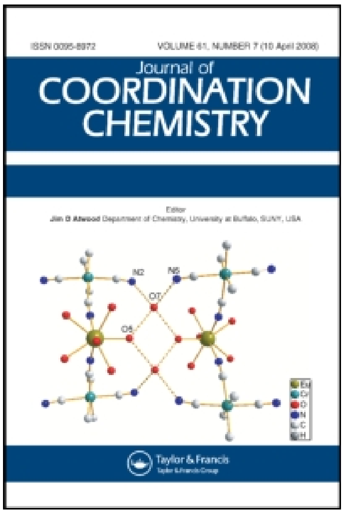

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Crystal Structure and Triboluminescence Spectrum of A <i>µ</i>2-(ONC$_5$H$_5$) Bridging Dinuclear Europium(III) Complex

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CRYSTAL STRUCTURE AND TRIBOLUMINESCENCE SPECTRUM OF A μ_2-(ONC_5H_5) BRIDGING DINUCLEAR EUROPIUM(III) COMPLEX

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The crystal structure and triboluminescence spectrum of a μ_2-(ONC_5H_5) bridging dinuclear europium(III) complex, $Eu_2(TTA)_6(PyO)_2$ where HTTA = 2-thenoyltrifluoroacetone, PyO = pyridine N-oxide, are reported. It is centrosymmetric and two Eu(III) atoms are bridged by two pyridine oxide oxygen atoms. The Eu……Eu distance is 4.2137(9) Å. The triboluminescence maximum is similar to that of the photoluminescence and the disorder of the thienyl rings and CF_3 groups may be responsible for its triboluminescent activity. The complex crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 12.239(1)$, $b = 12.614(2)$, $c = 14.048(2)$ Å, $\alpha = 110.31(1)$, $\beta = 112.05(l)$, $\gamma = 99.23(1)°$, $V = 1776.6(4)$ Å^3 and $Z = 2$. The structure was refined by full-matrix least squares methods to $R = 0.0451$ and $R_w = 0.1170$.

Keywords: Triboluminescence; Dinuclear europium(III) complex; Disorder

INTRODUCTION

Triboluminescence is the emission of light produced during mechanical action on solids. Although it is an old phenomenon, its mechanism is not

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well understood. In recent years, triboluminescent compounds have received more attention since they can transfer mechanical stress into light radiation and can be used for optical sensors [1], for example, artifical skin to sense mechanical stress by visible light emission. The triboluminescent activity of $[Eu(TTA)_3(PyO)]_n$ (HTTA = 2-thenoyltrifluoroacetone, PyO = pyridine N-oxide) was described [1a], however to the best of our knowledge, its crystal structure and triboluminescence spectrum have not been reported. In continuation of our interest in searching for a clear pattern of triboluminescent activity as a function of crystal structure [2], we re-investigated this complex. In the course of the re-investigation, an unexpected μ_2-(ONC_5H_5) bridging dinuclear europium(III) complex, $Eu_2(TTA)_6(PyO)_2$ (**1**), was obtained. In this paper, we report the crystal structure, photoluminescence spectrum and triboluminescence spectrum of the first dinuclear lanthanide triboluminescent complex **1**.

EXPERIMENTAL

Preparation of Complex 1

All chemicals were of analytical grade and were used without further purification. Complex **1** was prepared according to the literature methods [1a]. Purification was accomplished by recrystallization. Single crystals suitable for x-ray crystallography were obtained from MeCN-EtOH. Found: C,38.37; H,1.96; N,1.31. Calc. For $Eu_2C_{58}H_{34}F_{18}N_2O_{14}S_6$(%): C,38.24; H,1.88; N,1.54. The medium-IR showed peaks at 3450 (w), 3134 (w), 1623 (s), 1602 (s), 1577 (s), 1539 (s), 1506 (s), 1479 (m), 1414 (s), 1358 (m), 1310 (s), 1247 (s), 1230 (s), 1185 (s), 1140 (s), 1084 (m), 1062 (m), 1035 (w), 1026 (w), 935 (m), 861 (w), 835 (m), 787(m), 770 (m), 750 (w), 719 (m), 692 (w), 681 (m), 641 (m), 604 (w), 581 (m), 559 (m), 520 (w), 493 (w), 462 (m), 420 (w).

Physical Measurements

Elemental analysis was performed on a Perkin-Elmer 240C analytical instrument. The IR spectrum was recorded on a Nicolet FT-IR 170sx spectrophotometer by KBr pellet in the range of 4000 – 400cm^{-1}. 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 on an AB2 Luminescence Spectrometer (Version 4.00). A Xe lamp was used with $\lambda_{ex} = 397$ nm.

Crystallography

X-ray crystallography was performed using a Siemens P4 diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293K. Crystal data are listed in Table I. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS [3]. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL-97 [4]. All the non-hydrogen atoms were refined anisotropically. The terminal CF_3 groups are disordered due to free rotation about the C—C bonds. The S(1), S(2) and S(3) atoms and the ortho-carbon C(6), C(14) and C(22) atoms were also found to be disordered. The occupancies of S(1), S(2), S(3), C(6), C(14) and C(22) atoms were refined to 0.728, 0.821, 0.900, 0.27, 0.18 and 0.10, respectively. All computations were

TABLE I Crystal data and structure refinement for **1**

Formula	$C_{29}H_{17}EuF_9NO_7S_3$
Formula weight	1921.16
Crystal size (mm)	0.48 × 0.40 × 0.26
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	12.239(1)
b (Å)	12.614(2)
c (Å)	14.048(2)
α (°)	110.31(1)
β (°)	112.05(1)
γ (°)	99.23(1)
V (Å^3)	1776.6(4)
Z	2
Dcalc (Mg/m^3)	1.702
μ (mm^{-1})	2.032
Reflections	8924
Unique reflections	7819
Data/restraints/parameters	7819/0/454
R,wR[I > 2σ(I)]	0.0451, 0.1170
w^{-1}	$\sigma^2(F_0)^2 + (0.0678P)^2$
Goodness-of-fit on F^2	1.025
ρ_{max}, ρ_{min} (e Å^{-3})	1.130, −1.456

$P = (F_0^2 + 2F_c^2)/3$.

TABLE II Selected bond lengths [Å] and angles [°] for **1**

Eu(1)—O(1)	2.365(4)
Eu(1)—O(2)	2.389(4)
Eu(1)—O(3)	2.382(4)
Eu(1)—O(4)	2.371(4)
Eu(1)—O(5)	2.382(3)
Eu(1)—O(6)	2.369(4)
Eu(1)—O(7)	2.466(3)
Eu(1)—O(7)#1	2.452(4)
Eu(1)—Eu(1)#1	4.2137(9)
O(1)—Eu(1)—O(2)	71.35(13)
O(3)—Eu(1)—O(4)	71.06(13)
O(5)—Eu(1)—O(6)	71.09(13)
O(7)#1—Eu(1)—O(7)	62.10(12)
Eu(1)#1—O(7)—Eu(1)	117.90(12)
N(1)—O(7)—Eu(1)#1	121.7(3)
N(1)—O(7)—Eu(1)	120.3(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$.

carried out using the SHELXTL-97 [4]. Selected bond lengths and angles are listed in Table II.

RESULTS AND DISCUSSION

The *ORTEP* drawing of **1** is shown in Figure 1. The two Eu(III) atoms are bridged by two pyridine oxide oxygen atoms. Each europium is eight-coordinate with six oxygen atoms from three HTTA anions and two oxygen atoms from the bridging pyridine oxides. The Eu……Eu distance is 4.2137(9) Å. The two europium atoms and two bridging pyridine oxide oxygen atoms are coplanar. The angles of Eu(1)—O(7)—Eu(1A) and O(7)—Eu(1)—O(7A) are 117.90(12)° and 62.10(12)°, respectively. The Eu—O(TTA) distances (2.365–2.389 Å) are somewhat shorter than those of the Eu—O (pyridine oxide) (2.452 & 2.466 Å) and of Eu(TTA)$_4$dmp (2.368–2.415 Å) (dmp = 1,4-dimethylpyridinium) [2a]. The coordination geometry of the Eu(III) atom is best described as a strongly distorted square-antiprism. The least-squares plane fitted to atoms O(1), O(2), O(5) and O(6) has a mean deviation of 0.2824 Å, whereas another face defined by O(3), O(4), O(7) and O(7A) has a mean deviation of 0.2872 Å. The dihedral angle between these two least-squares planes is *ca.* 4.7°.

The photoluminescence emission spectrum of solid-state **1** is shown in Figure 2. The emission is typical of europium centered transitions from

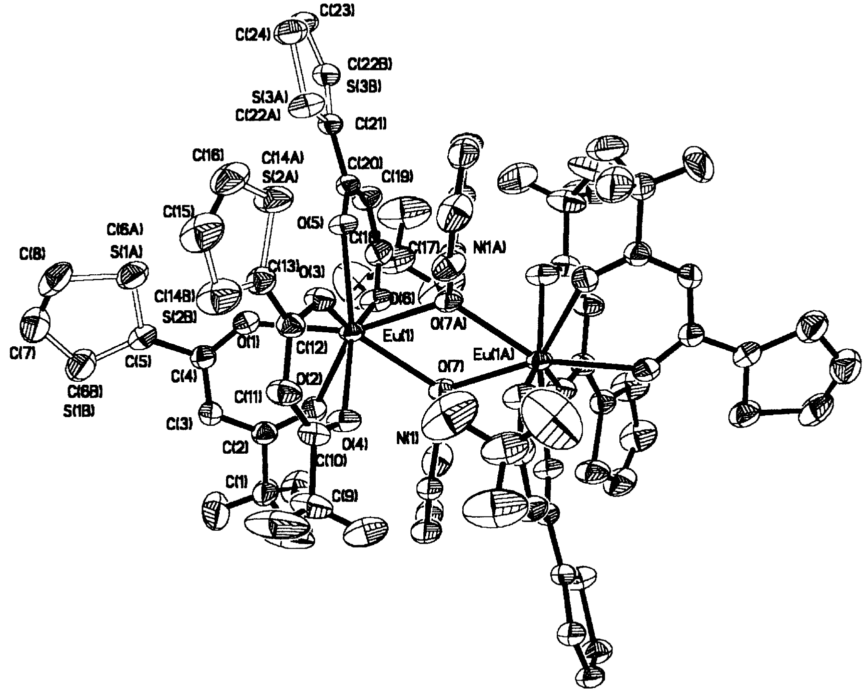

FIGURE 1 *ORTEP* drawing of **1** (Symmetry code: #1 −x, −y, −z).

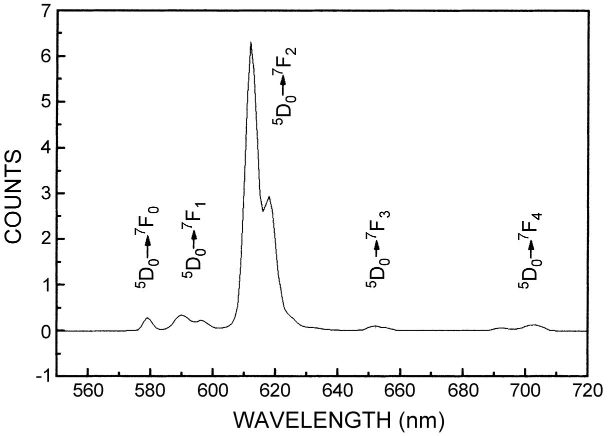

FIGURE 2 Emission spectrum ($\lambda_{ex} = 397\,nm$) of solid **1** at room temperature.

$^5D_0$ levels to the lower $^7F_{0-4}$ levels of the ground-state multiplet. The main emission occurs, 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 symmetry of **1** was assigned as C_1 [5].

Crude **1** exhibits red triboluminescence in darkness. After recrystallization from different solvents such as MeOH, EtOH, MeCN or Me_2CO, its triboluminescence was somewhat strengthened but was decreased upon grinding in air. The triboluminescence spectrum of complex **1** is shown in Figure 3. The maxima (612.36 and 617.48 nm) in the triboluminescence spectrum are essentially at the same wavelengths as those in the photoluminescence spectrum (612.00 and 617.78 nm). There are no detectable dinitrogen emissions. The triboluminescence emission is weaker than that of the photoluminescence so only the part of the triboluminescence emission corresponding to the most intense photoluminescence emission was observed. Therefore, the triboluminescence is assigned to the same excited state as the photoluminescence. The part emission observed in the triboluminescence spectrum is centered on the transition of europium from $^5D_0$ to $^7F_2$ levels. There is no apparent difference in triboluminescence between dinuclear complex **1** and other mononuclear complexes studied before [2].

Theory predicts that the crystals exhibiting triboluminescent activity should have a noncentrosymmetric space group or be polar and piezoelectric since only such materials can generate opposite charges on the opposing faces of cracks perpendicular to the polar axis [6]. Our crystallographic

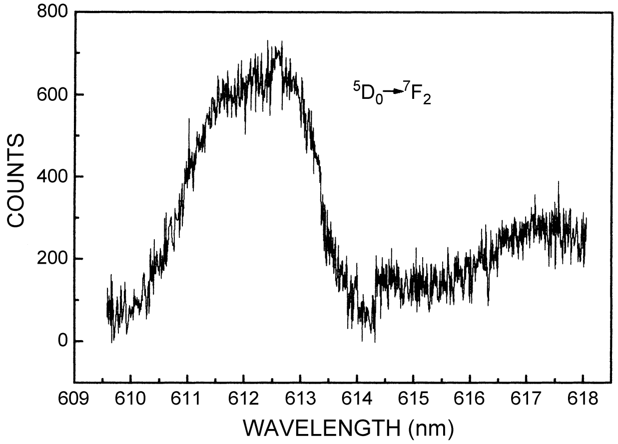

FIGURE 3 Triboluminescence spectrum of **1** at room temperature.

data for complex **1**, which is centrosymmetric ($P\bar{1}$), offers no obvious structural basis for triboluminescent activity. Several theories are raised to explain why the crystal having a centrosymmetric space group still exhibits triboluminescent activity. The importance of trace dopants in determining triboluminescent activity was proven for saccharin [7] and anthracene derivatives [8]. Random impurities may create local dissymmetry. Local cracks may occur in noncentrosymmetric environments in a crystal which is still overall centrosymmetric. Since complex **1**, recrystallized from the crude products, still exhibits triboluminescence, impurities seem not to be responsible for its triboluminescence. Rheingold and King suggest that ionic compounds may permit charge separation by partial fracture along planes with opposite charges [6]. The complex **1** is non-ionic, and could not obtain the local piezoelectricity essential to its triboluminescent activity in weak interionic interactions capable of deformation on application of pressure. In the discussion of the relation between the structure and triboluminescent activity of triethylammonium tetrakis(dibenzoylmethanato)europate, Sweeting and Rheingold suggested the disorder of phenyl rings and cation may provide a sufficient source of localized polarity to produce the observed activity [9]. We recently found that disorders may correlate with the tribolummescent activities in centrosymmetric $Eu(TTA)_4dmp$ [2a], $Eu(TTA)_3 \cdot bipy$ [2c] and $Eu(DBM)_3dmbp \cdot H_2O$ [2c] (DBM = dibenzoylmethane, dmp = 1 ,4-dimethylpyridnum, bipy = 2,2'-bipyridine, dmbp = 4,4'-dimethyl-2,2'-bipyridine). A similar effect is also evident in centrosymmetric **1**. There is disorder of all thienyl rings and all 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, namely, the disorder may provide local dissymmetry needed to support charge separation. Therefore, we think that the disorder of the thienyl rings and the CF_3 groups may play an important role in the triboluminescence of centrosymmetric **1**. This result further confirms the theory of Sweeting.

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