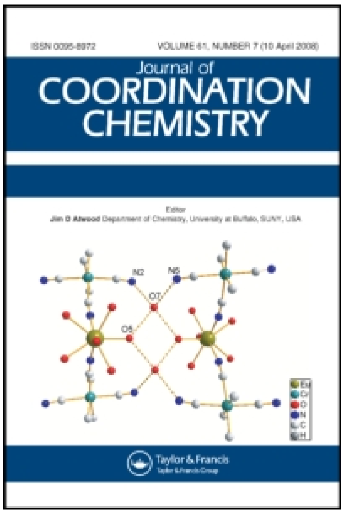

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CRYSTAL STRUCTURE AND PHOTOLUMINESCENCE OF 1,7-DIMETHYLQUINOLIUM TETRAKIS-(2-THENOYLTRIFLUOROACETONATO)-EUROPATE

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The crystal structure and photoluminescence spectrum of 1,7-dimethylquinolium tetrakis (thenoyltrifluoroacetonato)europate (**1**) are reported. Complex **1** is centrosymmetric and exibits no triboluminescence. Disorder of the thienyl rings may not be responsible for triboluminescence in centrosymmetric materials. The photoluminescence studies showed that the local symmetry of Eu(III) is C_s or C_2. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with cell parameters, $a=10.778(3)$, $b=21.903(5)$, $c=20.470(4)\,Å$; $\beta=99.25(2)°$; $V=4770(2)\,Å^3$ and $Z=4$. The structure was refined by full-matrix least squares to $R=0.0713$ and $R_w=0.1090$.

Keywords: Europate (III); HTTA; 1,7-dimethylquinolium; photoluminescence

INTRODUCTION

Luminescent lanthanide ions are being extensively used to solve analytical and structural problems, especially to probe local structures in crystals, glasses and solutions.[1] Since Eu(III) displays intense luminescence,

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information can be obtained by analyzing high-resolution, laser-excited excitation and emission spectra of Eu(III)-containing compounds. On the other hand, complexes of the lanthanide elements exhibiting brilliantly triboluminescent properties can be used for optical sensors sensitive to impact, tension or pressure.[2] In order to construct a theory of triboluminescence, physicists and chemists have searched for a clear pattern of triboluminescence activity as a function of crystal structure. Sweeting[3] suggested that disorder plays an important role in triboluminescent activity of centrosymmetric materials. Recently we found that disorder of three thienyl rings and three CF_3 groups in 1,4-dimethylpyridinium tetrakis(2-thenoyltrifluoroacetonato)europate (**2**)[4] may be responsible for its triboluminescent activity. However, it is not clear which disorder is more important to the triboluminescence between thienyl rings and CF_3 groups. Continuing our interest in the relationship between disorder and triboluminescent activity, we report the crystal structure and photoluminescence spectrum of complex **1** which is centrosymmetric and not triboluminescent.

EXPERIMENTAL

Materials and Methods

All chemicals were analytical grade and used without further purification. Iodine 1,7-dimethylquinolium was prepared according to the literature method.

Preparation of Complex 1

1.04 g of HTTA (2-thenoyltrifluoroacetone) and 0.332 g iodine 1,7-dimethylquinolium were dissolved in 20 mL of ethanol and the mixture was heated to boiling. Then 0.187 g NaOH in 10 mL water was added. Under vigorous stirring, a $Eu(NO_3)_3$ (1.17 mmol) solution was added dropwise and the resultant mixture was refluxed for 3 h with stirring. After hot filtration, the filtrate was allowed to stand at room temperature for several days. Orange single crystals suitable for X-ray diffraction were obtained. Anal. Calcd. for $EuC_{43}H_{28}F_{12}NO_8S_4$ (%): C, 43.20; H, 2.35; N, 1.17. Found: C, 43.63; H, 2.78; N, 1.52. The IR of **1** showed peaks at 3091(w), 1639(s), 1605(s), 1576(m), 1537(s), 1522(s), 1481(m), 1452(m), 1441(m), 1413(s), 1383(w), 1370(w), 1355(m), 1307(s), 1249(s), 1231(s), 1192(s), 1180(s), 1135(s), 1119(s), 1084(m), 1060(m), 1032(m), 1014(m), 969(w), 934(m), 910(w), 860(m), 843(m), 785(m), 768(m), 751(m), 719(m), 712(m), 692(w), 681(m), 642(m), 579(m), 491(w), 457(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 as a KBr pellet in the range of 4000–400 cm^{-1}. The photoluminescence spectrum was obtained using an Acton Research Corporation (ARC) SpectraPro-750, Santa Barbara Instruments Group (SBIG) CCD Detection System and Nd:YAG laser. 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 is ±0.1 nm with the 1200 grooves/mm grating. The 355 nm laser line of a Nd:YAG laser with 20 ns pulse width was used to pump the sample.

Crystallography

The intensities were collected on a Siemens P4 four-circle diffractometer with monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS.[5] A total of 8874 reflections, of which 8397 reflections were unique ($R_{\text{int}} = 0.1129$), were collected in the range $3.5 \leq 2\theta \leq 50°$ using a $\omega/2\theta$ scan mode with a variable scan speed 5.0–50.0° min^{-1} in ω. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL version 5.0.[6] Complex **1** crystallizes in the monoclinic space group P2$_1$/c with $a =$ 10.778(3), $b = 21.903(5)$, $c =$ 20.470(4) Å, $\beta = 99.25(2)°$, $V = 4770(2)$ Å^3, $Z = 4$; $Mw = 1194.86$, $D_{\text{calc}} =$ 1.664 g cm^{-3}, $F(000) = 2368$ and $\mu = 1.588$ mm^{-1}. The three thienyl rings are two-fold disordered about the bonds joining the rings to the backbone of the chelate to different degrees. The occupancy of S(1), S(1′), S(3), S(3′), S(4) and S(4′) were refined to 0.685, 0.315, 0.855, 0.145, 0.848 and 0.152, respectively.

All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (C–H, 0.96 Å) assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached (1.5 times for methyl groups) and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations. All computations were carried out on a PC-586 computer using the SHELXTL -Pc program package.[6] The final cycle of refinement included 625 parameters and converged with unweighted and weighted agreement factors of $R = 0.0713$ and $R_w = 0.1090$; GOF = 0.808 (on F^2) (The weighting scheme was $w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$,

TABLE I Selected bond distances (Å) and angles (°) for **1**

Eu–O(1)	2.397(5)	Eu–O(2)	2.353(5)
Eu–O(3)	2.357(5)	Eu–O(4)	2.432(5)
Eu–O(5)	2.378(5)	Eu–O(6)	2.401(5)
Eu–O(7)	2.378(5)	Eu–O(8)	2.404(3)
O(1)–C(5)	1.230(10)	O(2)–C(7)	1.215(8)
O(3)–C(13)	1.225(9)	O(4)–C(15)	1.228(8)
O(5)–C(23)	1.233(7)	O(6)–C(21)	1.227(9)
O(7)–C(29)	1.233(8)	O(8)–C(31)	1.250(8)
O(1)–Eu–O(2)	70.4(2)	O(3)–Eu–O(4)	71.2(2)
O(5)–Eu–O(6)	70.3(2)	O(7)–Eu–O(8)	70.3(2)

$P = (F_0^2 + 2F_c^2)/3$, $a = 0$, $b = 0$). The maximum and minimum peaks on the final difference Fourier map corresponded to 0.549 and $-0.880\,e\text{Å}^{-3}$, respectively. Selected bond lengths and angles are listed in Table I.

DISCUSSION

Photoluminescence Spectrum

Complex **1** is highly luminescent in the solid state. Its photoluminescence spectrum at room temperature is shown in Figure 1. The complex exhibits strong red luminescence which arises from a transition from the $^5D_0$ level to the $^7F_{0-4}$ levels and has been assigned in Table II. There are some weak bands which result from the vibrational transition of electron–phone couple according to its IR spectrum. The transition from $^5D_0 \rightarrow {}^7F_0$ has been observed. In 32 point groups there are only C_s, C_n and C_{nv} in which the $^5D_0 \rightarrow {}^7F_0$ transition can be observed. Since complex **1** belongs to the monoclinic system, the local symmetry of Eu(III) may be C_s or C_2 after it is excited.[7] The electric dipole transitions $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ are more intense than the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ reflecting the lower site symmetry of Eu(III).

Descriptions of the Structure

An ORTEP drawing of complex **1**, with the atom-numbering scheme, is shown in Figure 2. It is a tetra-bidentate, eight-coordinated Eu(III) complex containing four HTTA anionic ligands. The average Eu–O distance in **1** (2.39(2) Å) is in accordance with that of **2** (2.39(1) Å), although in **1** a slightly greater range (2.353–2.432 Å for **1** and 2.368–2.415 Å for **2**) of Eu–O distances reflects the lower symmetry of **1**. The average C–O bond in **1**

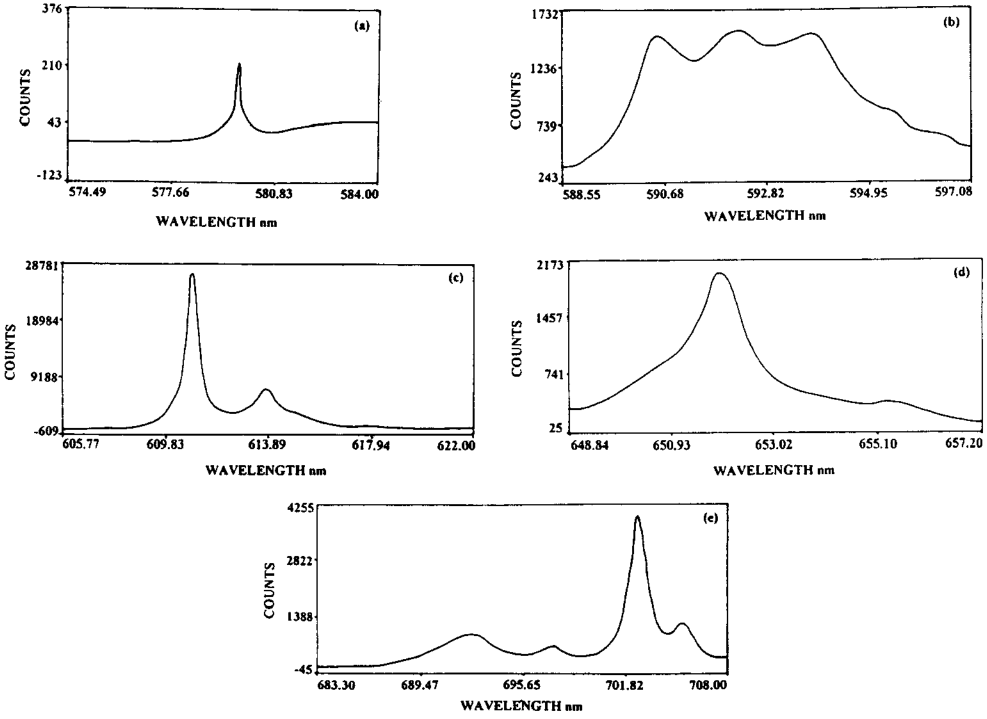

FIGURE 1 (a)–(e) Emission spectrum ($\lambda_{ex} = 355\,nm$) of solid **1** in the range 550–720 nm at room temperature.

TABLE II Luminescence spectral data of the complex **1**

λ (nm)	*Assignment*
579.70	$^5D_0 \rightarrow {}^7F_0$
590.50	$^5D_0 \rightarrow {}^7F_1$
592.22	$^5D_0 \rightarrow {}^7F_1$
593.83	$^5D_0 \rightarrow {}^7F_1$
599.81	vibr
603.59	vibr
610.82	$^5D_0 \rightarrow {}^7F_2$
613.78	$^5D_0 \rightarrow {}^7F_2$
614.92	$^5D_0 \rightarrow {}^7F_2$
626.41	vibr
631.20	vibr
651.89	$^5D_0 \rightarrow {}^7F_3$
692.53	$^5D_0 \rightarrow {}^7F_4$
697.29	$^5D_0 \rightarrow {}^7F_4$
702.60	$^5D_0 \rightarrow {}^7F_4$
705.26	$^5D_0 \rightarrow {}^7F_4$

vibr: electronic–vibrational transition.

(1.230 Å) is shorter than those in **2** (1.241 Å), reflecting the lower π atom delocation of the C–O double bond in **1**. The O–Eu–O angles within a chelate ring have averages similar to **1**, 70.55° and **2**, 72.60°. The 1,7-dimethylquinolium cation does not coordinate with Eu(III). Difference electron density maps computed in the plane of the fluorine atoms in each CF_3 group gave no indication of disorder. Three thienyl rings are two-fold disordered. The bond distances and angles within these rings are anomalous due to the disorder. It is interesting to note that 4-methylpyridium tetrakis(thenoyltrifluoroacetonato)europate[8] and N-ethylpyridinium tetrakis(thenoyltrifluoroacetonato)europate[9] crystallized in the centric space group $P\bar{1}$ and 3,6-di(dimethylamine)-diphenyliodonium tetrakis(thenoyltrifluoroacetonato)europate[10] crystallizes in the centric space group $P2_1/n$. These complexes exhibit no disorder of the thienyl rings and CF_3 groups and exhibit no triboluminescent activity. Three out of four thienyl rings and three of the four CF_3 groups display equally occupied alternative positions in centrosymmetric complex **2**. The observed triboluminescent emission may be correlated with the disorders of thienyl rings and CF_3 groups.[4] Sweeting[3] thought that disorder provided 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. The centrosymmetric **1** also exhibits disorder of three thienyl rings but no triboluminescence. Comparing the structures and triboluminescent activities of complex **1** and **2**, we believe that disorder of the CF_3 groups plays an important role in

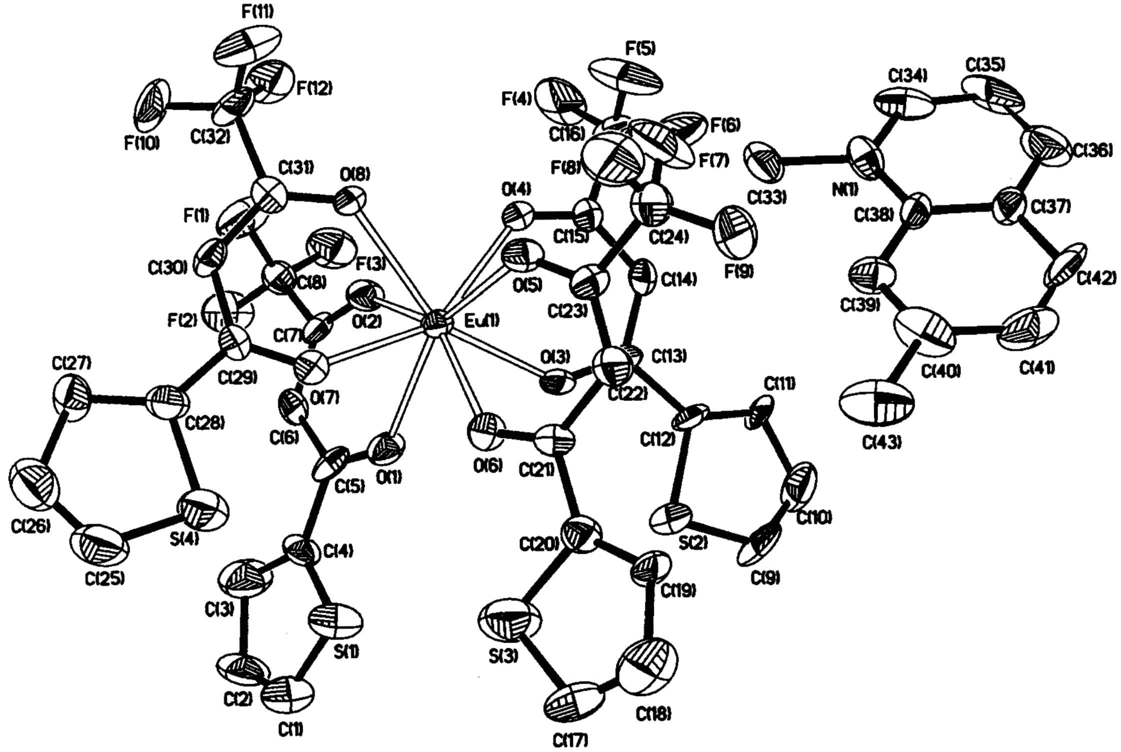

FIGURE 2 An ORTEP drawing of complex **1** with atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

triboluminescence for centrosymmetric complex **2** *i.e.*, the disorder of thienyl rings is not responsible for the triboluminescence. We are currently searching for other materials to confirm this suggestion.

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References

[1] D. Plancherel, L.P. Jin and J.C.G. Bünzli, *Helv. Chim. Acta* **70**, 1807 (1987).
[2] G. Veronique, *PCT Int. Appl. WO* 96 20, 942.
[3] L.M. Sweeting and A.L. Rheingold, *J. Am. Chem. Soc.* **109**, 2652 (1987).
[4] X.F. Chen, S.H. Liu, C.Y. Duan, Y.H. Xu, X.Z. You and J. Ma, *Polyhedron* **17**, 1883 (1998).
[5] Siemens, XSCANS (Version 2.1), Siemens Analytical X-ray Instruments Inc. Madison, USA, 1994.
[6] Siemens, SHELXTL (Version 5.0), Siemens Industrial Automation, Inc., Analytical Instrumentation, USA, 1995.
[7] C.H. Huang, *Coordination Chemistry of Rare Earth*, Perking, Science Publishing Co., 1997.
[8] A.Z. Wei, M.K. Teng, J.B. Dai and T.C. Liang, *J. Struct. Chem. (Chinese)*, **2**, 237 (1983).
[9] C.H. Huang, X.Y. Zhu, F.Y. Guo, J.Q. Song, Z.H. Xu and C.S. Liao, *Acta Sientiarum Naturalium Universitatis Pekinensis* **28**, 428 (1992).
[10] B.T. Chen, Y.G. Zhang, L. Gao and M.Z. Wang, *Acta Chimica Sinica* **55**, 553 (1997).