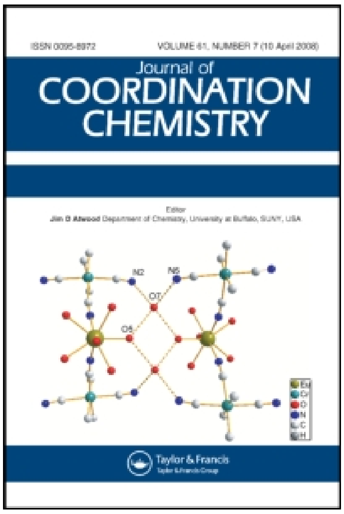

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CRYSTAL STRUCTURES AND TRIBOLUMINESCENT ACTIVITIES OF SAMARIUM(III) COMPLEXES

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CRYSTAL STRUCTURES AND TRIBOLUMINESCENT ACTIVITIES OF SAMARIUM(III) COMPLEXES

XIAO-FENG CHEN[a], XU-HUI ZHU[a], WEI CHEN[b], JAGADESE J. VITTAL[c], GOEK-KHENG TAN[c], JUN WU[d] and XIAO-ZENG YOU[a,*]

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The triboluminescence spectra and crystal structures of 1,2-dimethylpyridinium tetrakis(2-thenoyltrifluoroacetonato)samarium(III) (**1**) and 1,2,6-trimethylpyridinium tetrakis(2-thenoyltrifluoroacetonato)samarium(III) (**2**) were determined. The triboluminescent maximums are similar to those of the photoluminescence. Complex **1** is centrosymmetric and the triboluminescent emission may correlate with the disorder of all S atoms, all CF_3 groups and the cation. The triboluminescent activity of complex **2** may correlate with its noncentrosymmetric space group. Complex **1** crystallizes in the monoclinic space group $P2_1/a$ with cell parameters $a = 19.874(2)$ Å, $b = 22.922(2)$ Å, $c = 21.188(1)$ Å, $\beta = 108.126(6)°$, $V = 9173(1)$ Å^3; $Z = 8$; $R = 0.0758$ and $R_w = 0.1315$. Complex **2** crystallizes in the monoclinic space group Pn with cell parameters $a = 11.2808(6)$ Å, $b = 11.0199(5)$ Å, $c = 18.4336(9)$ Å, $\beta = 108.126(6)°$; $V = 2285.28(19)$ Å^3; $Z = 4$; $R = 0.0347$ and $R_w = 0.0900$. All the structures were refined by full-matrix least squares methods.

Keywords: Samarium complexes; HTTA; Triboluminescence; Disorder

INTRODUCTION

Triboluminescence is the emission of light produced during mechanical action on solids. Although the phenomenon of triboluminescence is well

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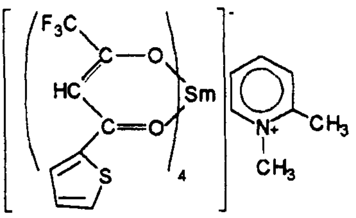
known, its cause cannot be completely accounted for and no predictions can be made concerning the occurrence of particularly intense triboluminescent compounds. In recent years, complexes of the lanthanide elements (Eu, Tb, Sm and Dy) exhibiting brilliantly triboluminescent properties have received attention since the triboluminescent properties make these complexes suited for use as optical sensors sensitive to impact tension or pressure [1]. Furthermore, for the construction of a predictive theory of triboluminescence, extensive searching for a clear pattern of triboluminescent activity as a function of crystal structure has been under way [2, 3]. Over the years, the strong correlation of noncentrosymmetric crystal structure with triboluminescence has led most observers to conclude that the piezoelectric properties of noncentrosymmetric crystals are always the source of triboluminescence. However, there exist many centrosymmetric crystals which are triboluminescent and many noncentrosymmetric crystals which are not. Sweeting suggested that a noncentrosymmetric crystal structure is necessary for tribophotoluminescence in pure covalent compounds and disorder plays an important role in triboluminescence activity of centrosymmetric materials [2a, 4]. We found recently that the disorder of the S atoms and F atoms in centrosymmetric 1,4-dimethylpyridinium tetrakis(2-thenoyltrifluoroacetonato)europate (III) [5] (3) may be responsible for its triboluminescent activity. Here we report the triboluminescent activities of two samarium complexes and their crystal structures.



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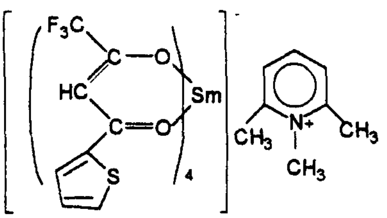

2

EXPERIMENTAL

Preparations

All chemicals were analytical grade and used without further purification. 1,2-dimethylpyridinium iodide and 1,2,6-trimethylpyridinium iodide were prepared according to the literature [6].

Complexes **1** and **2** were prepared by a procedure similar to that for 1,4-dimethylpyridinium tetrakis(2-thenoyltrifluoroacetonato)europate (**3**) [5]. Yellow products were obtained. Purification by recrystallization was accomplished by room temperature evaporation of solvent. Single crystals of **1** and **2** suitable for X-ray analysis were obtained from $C_2H_5OH—CH_3CN$. For complex **1**, found: C, 40.89; H, 2.38; N, 1.20. Calc. for $SmC_{39}H_{26}F_{12}NO_8S_4$(%): C, 40.94; H, 2.27; N, 1.22. IR(KBr) 1606 cm^{-1} (C=O). mp: 156–158°C. For complex **2**, found: C, 41.42; H, 2,48; N, 1.26. Calc. for $SmC_{40}H_{28}F_{12}NO_8S_4$(%): C, 41.49; H, 2.42; N, 1.21. IR(KBr) 1607 cm^{-1} (C=O). mp: 184–186°C.

Physical Measurements

The methods for physical measurements were described previously [7].

X-ray Crystallography

Intensity data collection for complex **1** was carried out on a Entraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 300 K. The intensity data for complex **2** were collected on a Siemens SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation at 293 K. Determinations of the crystal class, orientation matrix, and cell dimensions were performed according to established procedures; the intensity data were collected using the ω-scan method. For complex **1**, the data were corrected for Lorentz and polarization effects during data reduction using NRCVAX [8]. The structure was solved by Patterson methods and refined on F^2 by full-matrix least-squares methods using SHELXL93 [9]. All the nonhydrogen atoms were refined anisotropically. The sulfur atoms and the ortho-carbon atoms in all the five-membered rings were disordered and their multiplicities refined. The occupancy of each S atom was refined to 0.697, 0.910, 0.820, 0.505, 0.768, 0.789, 0.806 and 0.530 for S1 to S8, respectively. The cations are also disordered and were fixed as regular hexagons. Residual peaks were found around the terminal $—CF_3$ groups which were disordered due to free rotation about the C—C bonds. Some H atoms were generated geometrically and given riding mode while some were located from a difference map. All computations were carried out on a 486 computer using the SHELXTL93 package [9]. For complex **2**, the data were corrected for Lorentz and polarization effects using SADABS [10] during data reduction. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL Version 5.03 [11]. The methyl carbon atoms of the cations showed large thermal parameters. Isotropic thermal parameters were refined for C38, C39 and C40. All computations were carried out using the SHELXTL Version 5.03 package [11]. A summary of selected crystallographic data for the complexes **1** and **2** is given in Table I. Atomic coordinates of **1** and **2** are given in Tables II and III, respectively.

TABLE I Crystallographic data

Complex	**1**	**2**
Formula	$C_{39}H_{26}F_{12}NO_8S_4Sm$	$C_{40}H_{28}F_{12}NO_8S_4Sm$
M	1143.20	1157.22
Crystal size(mm)	0.36 × 0.36 × 0.2	0.5 × 0.5 × 0.18
Crystal system	Monoclinic	Monoclinic
space group	$P2_1/a$	Pn
a(Å)	19.874(2)	11.2808(6)
b(Å)	22.922(2)	11.0199(5)
c(Å)	21.188(1)	18.4336(9)
β(°)	108.126(6)	94.237(1)
V(Å^3)	9173(1)	2285.28(19)
Z	8	2
Dcalc(Mg/m^3)	1.656	1.682
μ(mm^{-1})	1.560	1.567
F(000)	4520	1146
Reflections	17537	11647
Unique reflections	17011	7006
Data/restrains/parameters	17011/0/1159	7006/200/581
$R, wR[I > 2\sigma(I)]$	0.0758, 0.1315	0.0347, 0.0900
W^{-1}	$\sigma^2(F_0)^2 + (0.0540P)^2$	$\sigma^2(F_0)^2 + (0.0624P)^2$
Goodness of fit on F^2	0.942	1.038
ρ_{max}, ρ_{min}(eA^3)	0.757, −0.630	0.590, −0.532

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

TABLE II Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2× 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U(eq)*
Sm(1)	2331(1)	1903(1)	37(1)	39(1)
S(1)	4354(2)	2488(2)	−792(2)	70(2)
C(16′)	4354(2)	2488(2)	−792(2)	70(2)
S(2)	1137(2)	1835(2)	−2427(2)	70(1)
C(26′)	1137(2)	1835(2)	−2427(2)	70(1)
S(3)	3734(2)	1918(2)	2506(1)	62(1)
C(36′)	3734(2)	1918(2)	2506(1)	62(1)
S(4)	64(2)	1617(2)	583(3)	86(2)
C(46′)	64(2)	1617(2)	583(3)	86(2)
F(11)	921(9)	3700(7)	−832(7)	246(9)
F(12)	1349(5)	3970(5)	−1505(8)	262(9)
F(13)	687(6)	3301(5)	−1650(7)	221(7)
O(11)	1645(3)	2695(3)	−614(3)	55(2)

TABLE II (Continued)

	x	y	z	$U(eq)$
O(12)	3049(3)	2382(3)	−484(3)	52(2)
C(11)	1235(7)	3540(9)	−1244(10)	110(5)
C(12)	1811(5)	3093(5)	−956(5)	59(3)
C(13)	2434(5)	3178(5)	−1084(6)	75(4)
C(14)	3024(5)	2819(5)	−838(5)	49(3)
C(15)	3664(5)	2940(4)	−1032(5)	60(3)
C(16)	3753(4)	3460(4)	−1487(4)	117(4)
S(1′)	3753(4)	3460(4)	−1487(4)	117(4)
C(17)	4531(6)	3359(7)	−1448(8)	114(6)
C(18)	4859(6)	2888(6)	−1123(6)	81(4)
F(21)	1816(7)	−244(4)	298(7)	186(6)
F(22)	1016(8)	144(5)	445(6)	189(6)
F(23)	891(6)	−308(4)	−420(4)	202(6)
O(21)	1860(3)	929(3)	109(3)	51(2)
O(22)	1729(3)	1570(3)	−1047(3)	57(2)
C(21)	1255(11)	45(7)	−33(7)	106(5)
C(22)	1458(5)	601(4)	−317(5)	42(2)
C(23)	1173(5)	670(4)	−992(5)	51(3)
C(24)	1318(5)	1153(5)	−1324(5)	48(3)
C(25)	981(4)	1219(4)	−2044(4)	47(2)
C(26)	508(4)	820(4)	−2517(4)	62(3)
S(2′)	508(4)	820(4)	−2517(4)	62(3)
C(27)	326(6)	1085(6)	−3173(5)	72(3)
C(28)	621(6)	1603(6)	−3190(5)	68(3)
F(31)	4236(7)	777(6)	−513(6)	195(6)
F(32)	3751(8)	142(5)	−318(8)	224(7)
F(33)	4663(7)	330(7)	356(4)	295(10)
O(31)	3198(3)	1207(3)	−99(3)	51(2)
O(32)	3113(3)	1653(3)	1106(3)	47(2)
C(31)	4155(12)	582(9)	−9(7)	133(8)
C(32)	3703(5)	947(5)	290(5)	56(3)
C(33)	3944(5)	990(4)	977(5)	59(3)
C(34)	3658(5)	1348(4)	1363(5)	47(2)
C(35)	3988(5)	1388(4)	2084(5)	48(2)
C(36)	4561(4)	999(4)	2505(4)	80(3)
S(3′)	4561(4)	999(4)	2505(4)	80(3)
C(37)	4693(6)	1226(6)	3181(6)	72(3)
C(38)	4295(6)	1679(6)	3230(5)	77(4)
F(41)	3083(6)	3577(4)	1684(6)	171(5)
F(42)	2101(5)	3930(4)	1566(6)	183(5)
F(43)	2579(8)	3961(4)	818(6)	190(6)
O(41)	2539(3)	2770(3)	721(3)	54(2)
O(42)	1398(3)	1987(3)	495(3)	53(2)
C(41)	2427(9)	3633(7)	1255(11)	116(6)
C(42)	2150(5)	3039(5)	972(5)	57(3)
C(43)	1506(5)	2898(4)	1030(5)	64(3)
C(44)	1151(5)	2381(5)	778(5)	50(3)
C(45)	455(5)	2235(4)	871(5)	53(3)
C(46)	31(3)	2696(3)	1215(3)	95(2)
S(4′)	31(3)	2696(3)	1215(3)	95(2)
C(47)	−647(6)	2262(7)	1106(6)	85(4)
C(48)	−619(6)	1746(6)	802(6)	77(4)
Sm(2)	7469(1)	512(1)	5031(1)	46(1)
S(5)	6218(2)	2086(2)	3394(3)	107(2)

TABLE II (Continued)

	x	*y*	*z*	*U(eq)*
C(56′)	6218(2)	2086(2)	3394(3)	107(2)
S(6)	5321(2)	−557(2)	2520(2)	69(1)
C(66′)	5321(2)	−557(2)	2520(2)	69(1)
S(7)	8820(2)	2001(2)	6736(2)	89(2)
C(76′)	8820(2)	2001(2)	6736(2)	89(2)
S(8)	9650(3)	−650(2)	7424(3)	96(2)
C(86′)	9650(3)	−650(2)	7424(3)	96(2)
F(51)	6545(8)	2139(5)	6609(5)	215(6)
F(52)	7223(5)	1427(5)	7012(4)	142(4)
F(53)	6145(5)	1299(5)	6630(4)	143(4)
O(51)	6931(4)	931(3)	5800(3)	66(2)
O(52)	6737(4)	1301(3)	4503(4)	77(2)
C(51)	6669(9)	1597(7)	6525(8)	97(4)
C(52)	6713(6)	1435(6)	5830(7)	77(4)
C(53)	6502(6)	1855(6)	5335(7)	91(4)
C(54)	6498(6)	1752(5)	4680(7)	74(4)
C(55)	6151(6)	2180(5)	4157(7)	83(4)
C(56)	5710(6)	2695(4)	4234(7)	148(6)
S(5′)	5710(6)	2695(4)	4234(7)	148(6)
C(57)	5448(11)	2951(8)	3567(12)	148(7)
C(58)	5710(10)	2669(8)	3131(9)	137(7)
F(61)	5052(5)	−985(5)	4670(4)	173(5)
F(62)	5502(5)	−489(4)	5536(5)	145(4)
F(63)	6011(5)	−1250(4)	5366(5)	144(4)
O(61)	6640(3)	−228(3)	5143(3)	57(2)
O(62)	6789(3)	174(3)	3949(3)	56(2)
C(61)	5642(7)	−790(8)	5070(7)	95(5)
C(62)	6091(6)	−430(5)	4740(5)	60(3)
C(63)	5857(5)	−385(5)	4066(5)	61(3)
C(64)	6218(5)	−83(4)	3684(5)	46(2)
C(65)	5956(5)	−85(4)	2956(4)	46(2)
C(66)	6218(3)	341(4)	2550(3)	74(3)
S(6′)	6218(3)	341(4)	2550(3)	74(3)
C(67)	5809(5)	147(5)	1862(5)	61(3)
C(68)	5354(5)	−287(5)	1792(5)	67(3)
F(71)	7784(6)	1464(5)	3126(5)	163(4)
F(72)	8578(9)	2089(5)	3545(5)	250(8)
F(73)	8808(6)	1236(6)	3447(5)	168(5)
O(71)	8042(4)	927(3)	4293(3)	67(2)
O(72)	8250(4)	1269(3)	5591(3)	67(2)
C(71)	8336(13)	1605(10)	3614(9)	136(7)
C(72)	8300(6)	1427(6)	4287(6)	74(3)
C(73)	8517(6)	1826(5)	4785(7)	84(4)
C(74)	8513(6)	1706(6)	5421(6)	71(3)
C(75)	8853(5)	2136(5)	5971(7)	72(3)
C(76)	9267(5)	2667(4)	5903(6)	123(5)
S(7′)	9267(5)	2667(4)	5903(6)	123(5)
C(77)	9516(8)	2897(7)	6602(9)	114(5)
C(78)	9318(8)	2584(7)	7072(9)	110(5)
F(81)	9877(5)	−932(5)	5203(5)	181(5)
F(82)	9353(5)	−394(5)	4379(5)	151(4)
F(83)	8913(6)	−1197(4)	4504(5)	157(5)
O(81)	8228(4)	−246(3)	4844(3)	63(2)
O(82)	8147(3)	101(3)	6074(3)	58(2)

TABLE II (Continued)

	x	*y*	*z*	*U(eq)*
C(81)	9257(10)	−767(9)	4843(8)	116(6)
C(82)	8803(6)	−422(5)	5195(6)	67(3)
C(83)	9102(6)	−393(5)	5893(6)	71(3)
C(84)	8740(5)	−145(4)	6290(5)	52(3)
C(85)	9060(5)	−180(4)	7031(5)	54(3)
C(86)	8796(3)	228(3)	7506(2)	77(2)
S(8′)	8796(3)	228(3)	7506(2)	77(2)
C(87)	9283(8)	−13(7)	8182(6)	97(5)
C(88)	9703(8)	−445(6)	8135(7)	97(5)
C(1)	3101(9)	1612(9)	7945(13)	254(17)
C(2)	2696(10)	1348(11)	6674(10)	227(14)
N(1)	2759(4)	1052(5)	7794(7)	147(7)
C(3)	2574(5)	957(6)	7114(6)	130(9)
C(4)	2215(6)	451(7)	6840(5)	174(12)
C(5)	2042(5)	40(5)	7248(9)	149(9)
C(6)	2227(6)	136(5)	7928(8)	221(15)
C(7)	2586(5)	642(7)	8201(4)	138(8)
C(91)	7596(11)	−1236(10)	6647(11)	252(17)
C(92)	8109(7)	−1457(8)	7892(11)	195(12)
N(2)	7390(5)	−798(5)	7040(5)	150(7)
C(93)	7703(5)	−977(5)	7693(7)	140(9)
C(94)	7607(6)	−651(7)	8212(4)	240(18)
C(95)	7197(7)	−147(7)	8078(6)	263(20)
C(96)	6884(6)	31(5)	7425(8)	262(17)
C(97)	6980(5)	−295(5)	6906(5)	127(7)

TABLE III Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for 2. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U(eq)*
Sm(1)	7499(1)	8192(1)	7367(1)	46(1)
S(1)	6445(2)	12294(2)	8460(2)	98(1)
S(2)	8425(3)	8279(2)	4066(2)	104(1)
S(3)	11830(2)	6816(2)	7196(2)	123(1)
S(4)	4771(3)	6653(3)	9274(2)	126(1)
F(1)	7808(6)	7433(5)	10426(2)	125(2)
F(2)	7712(5)	6058(4)	9650(3)	113(2)
F(3)	9363(5)	6931(5)	9920(4)	129(3)
F(4)	10937(5)	10739(6)	6829(4)	143(3)
F(5)	10613(6)	11041(6)	5711(4)	155(3)
F(6)	9606(7)	11947(4)	6468(4)	125(2)
F(7)	6021(7)	4488(5)	5995(3)	155(3)
F(8)	5830(5)	4022(5)	7058(3)	116(2)
F(9)	7165(5)	3199(4)	6502(5)	142(3)
F(10)	3537(6)	11316(6)	7086(3)	136(3)
F(11)	5003(6)	11450(6)	6449(5)	158(4)
F(12)	3589(4)	10253(5)	6152(3)	109(2)
O(1)	7371(3)	9941(3)	8170(2)	53(1)
O(2)	8266(4)	7658(4)	8571(2)	63(1)
O(3)	7564(4)	7877(4)	6050(2)	62(1)
O(4)	8772(4)	9698(4)	6907(2)	64(1)

TABLE III (Continued)

	x	*y*	*z*	*U*(*eq*)
O(5)	9292(4)	7055(4)	7218(3)	62(1)
O(6)	6933(4)	6162(4)	7091(2)	58(1)
O(7)	5793(4)	7709(4)	8044(2)	61(1)
O(8)	5793(4)	9270(4)	6856(2)	64(1)
C(1)	6167(9)	13311(7)	9090(8)	106(4)
C(2)	6316(9)	12968(9)	9781(7)	91(3)
C(3)	6723(5)	11679(4)	9881(3)	42(1)
C(4)	6834(5)	11255(5)	9083(3)	55(1)
C(5)	7232(5)	10036(5)	8835(3)	47(1)
C(6)	7468(5)	9125(5)	9352(3)	53(1)
C(7)	7959(6)	8034(5)	9182(3)	52(1)
C(8)	8211(7)	7125(6)	9802(4)	80(2)
C(9)	8054(8)	7164(9)	3588(4)	89(2)
C(10)	7597(8)	6190(10)	3950(5)	99(3)
C(11)	7523(5)	6399(5)	4749(3)	44(1)
C(12)	8025(5)	7688(7)	4849(3)	63(2)
C(13)	8144(6)	8296(5)	5560(4)	55(1)
C(14)	8925(7)	9281(7)	5660(4)	74(2)
C(15)	9169(5)	9878(5)	6296(4)	68(2)
C(16)	10097(8)	10903(8)	6315(5)	98(3)
C(17)	12947(8)	5887(11)	6991(6)	108(3)
C(18)	12617(7)	4846(8)	6716(5)	86(2)
C(19)	11344(5)	4623(6)	6605(4)	61(2)
C(20)	10813(5)	5784(6)	6906(3)	60(1)
C(21)	9537(5)	6038(5)	6959(3)	53(1)
C(22)	8680(5)	5144(5)	6759(3)	57(1)
C(23)	7473(5)	5284(5)	6839(3)	52(1)
C(24)	6647(6)	4243(5)	6598(4)	67(2)
C(25)	3556(18)	6612(15)	9741(9)	143(6)
C(26)	2806(14)	7440(20)	9623(10)	170(8)
C(27)	2970(7)	8159(6)	8995(5)	76(2)
C(28)	4201(6)	7760(7)	8764(4)	72(2)
C(29)	4842(6)	8224(5)	8159(4)	56(1)
C(30)	4379(6)	9231(7)	7743(4)	72(2)
C(31)	4886(5)	9645(5)	7140(3)	60(1)
C(32)	4261(6)	10685(7)	6711(5)	92(3)
N(1)	5038(7)	8577(9)	4248(10)	127(4)
C(33)	4724(9)	7650(10)	3898(5)	91(2)
C(34)	4447(11)	6615(10)	4205(7)	110(4)
C(35)	4480(13)	6675(14)	4977(9)	145(6)
C(36)	4816(11)	7610(20)	5342(7)	140(5)
C(37)	5160(10)	8623(17)	4984(14)	147(7)
C(38)	4620(16)	7671(19)	3073(11)	178(6)
C(39)	5340(16)	9663(16)	3736(10)	175(6)
C(40)	5790(30)	9870(30)	5003(17)	304(15)

RESULTS AND DISCUSSION

The ORTEP drawings of complexes **1** and **2** are shown in Figures 1 and 2, respectively. For the tetrakis chelates of β-diketones with trivalent

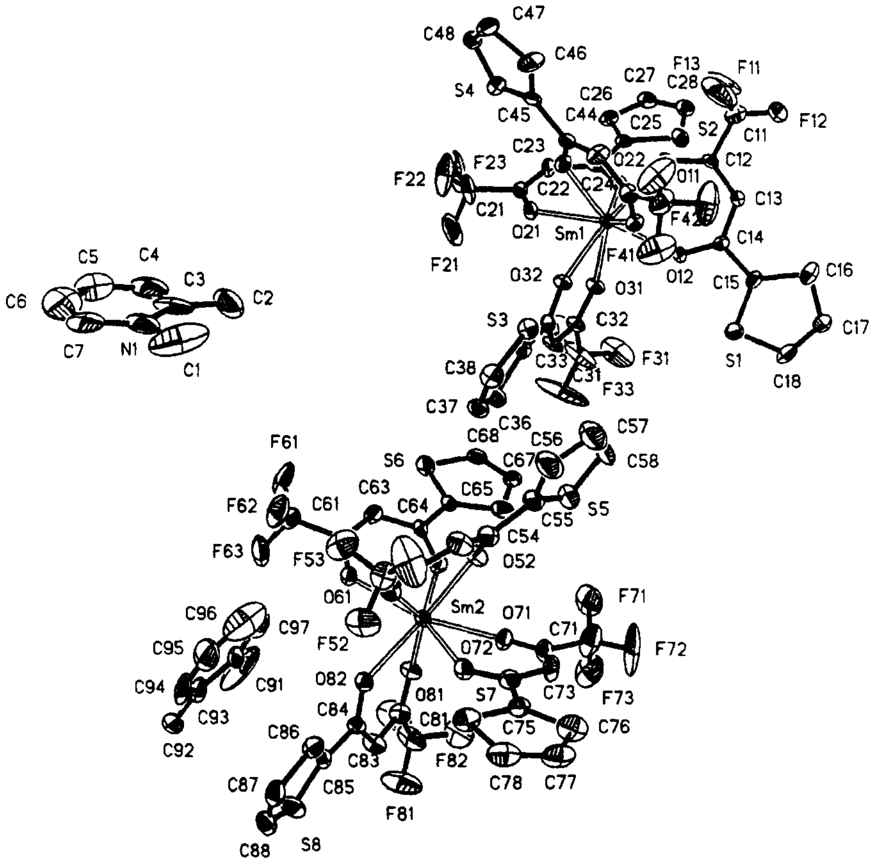

FIGURE 1 ORTEP drawing of **1**.

lanthanides, the chelate itself is an anion and a monovalent cation is required. The complex ions of **1** and **2** are tetrakis-bidentate, eight-coordinate Sm(III) complexes containing four HTTA anionic ligands and similar to that of TBASm(TTA)$_4$ (**4**) [12] [TBA = tetrabutylammonium cation, HTTA = 2-thenoyltrifluoroacetone]. The crystal structure of **1** is different from **4** in that it contains two asymmetric molecules. Each of the two asymmetric complex anions are eight coordinate with eight oxygen atoms from four ligands situated at the vertices of a square antiprism.

The triboluminescent activities of complexes **1** and **2** were tested upon initial crystallization. The crude products of **1** and **2** were triboluminescent at darkness. After recrystallization, the triboluminescent intensities of **1** and **2** are strengthened but decreased upon grinding in air. The photoluminescence spectrum of solid **1** at room temperature is very similar to that of **2**

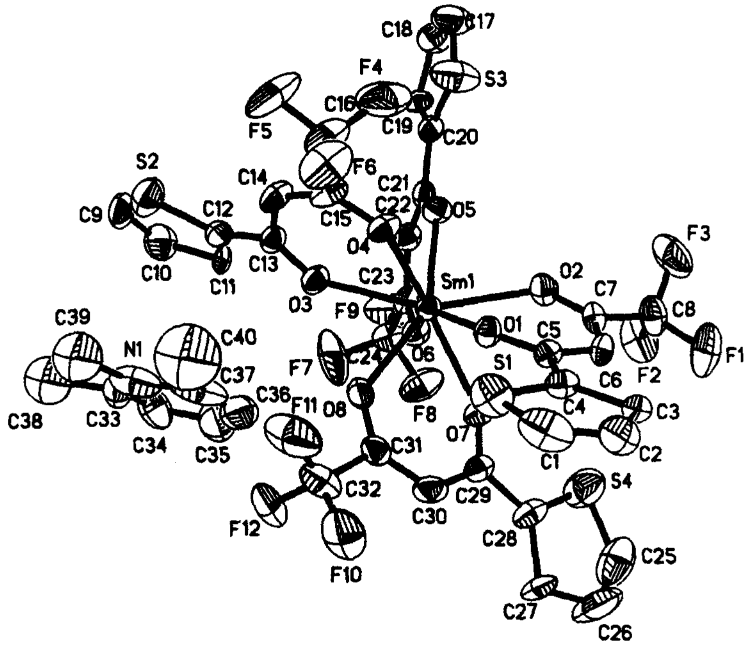

FIGURE 2 ORTEP drawing of **2**.

and is shown in Figure 3. The photoluminescence is typical of the samarium centered transitions from $^4G_{5/2}$ to the lower $^6H_{j/2}$ ($j = 5, 7, 9, 11$) levels [13] The triboluminescence spectra of **1** and **2** are given in Figures 4 and 5, respectively. The maximum and the splitting of the triboluminescence spectra (**1**: 645.39 and 651.5 nm; **2**: 645.51 and 651.23 nm) are very similar to those of their photoluminescence (*e.g.*, **1**: 645.80 and 651.92 nm). There are no detectable dinitrogen emissions. The triboluminescent emissions are weaker than those of photoluminescence so only parts of the emissions corresponding to the most intense photoluminescence were observed. The triboluminescence is assigned to the same excited state as the photoluminescence.

There is substantial evidence that charge separation created during fracture is the immediate precursor of the triboluminescent emission [14]. It is generally accepted that the primary event in the triboluminescence is the recombination of charges separated during fracture. So triboluminescent activity is usually assumed to be a consequence of crystal dissymmetry, *i.e.*, only piezoelectric (noncentrosymmetric) crystals may be triboluminescent because only such crystals can develop opposite charges on the opposing faces of a developing crack. However, the multitude of reports of

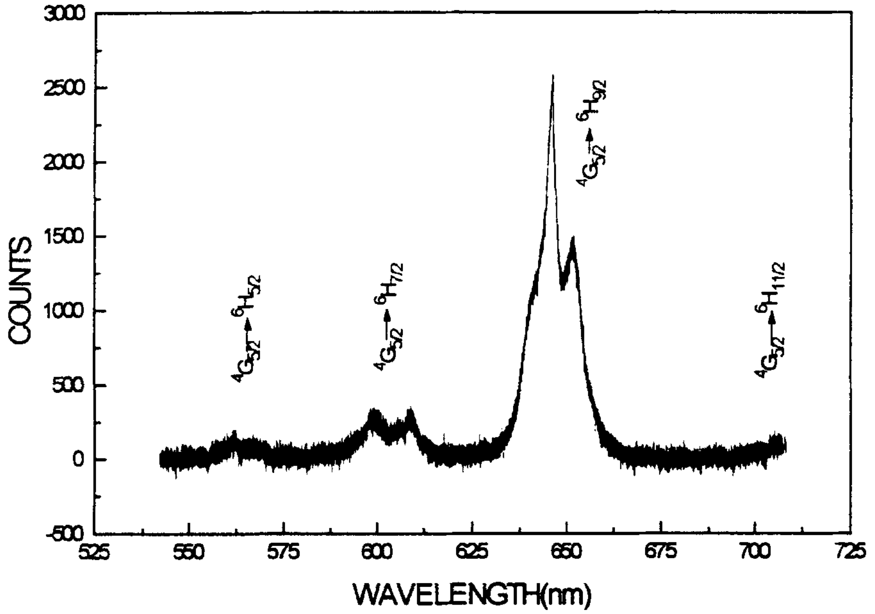

FIGURE 3 Emission spectrum ($\lambda_{ex} = 355$ nm) of solid 1 at room temperature.

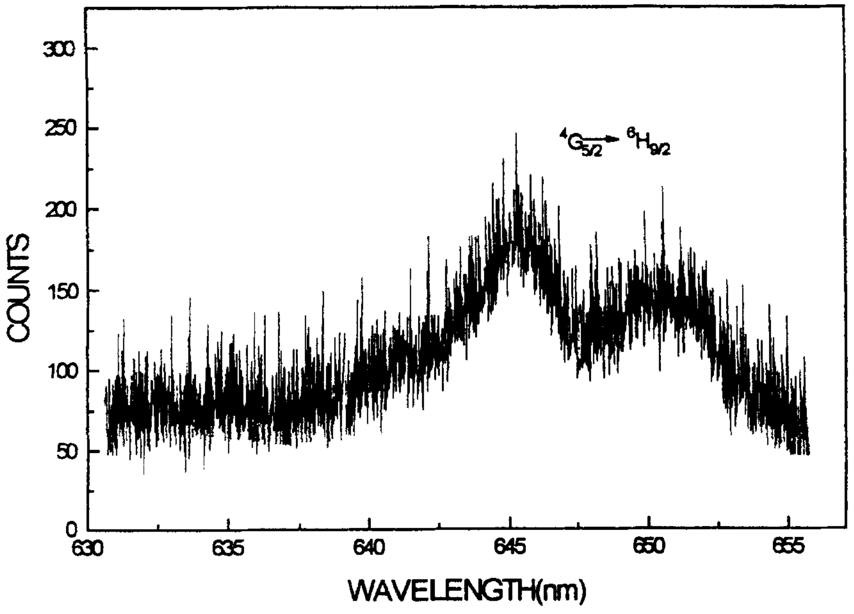

FIGURE 4 The triboluminescence spectrum of 1 at room temperature.

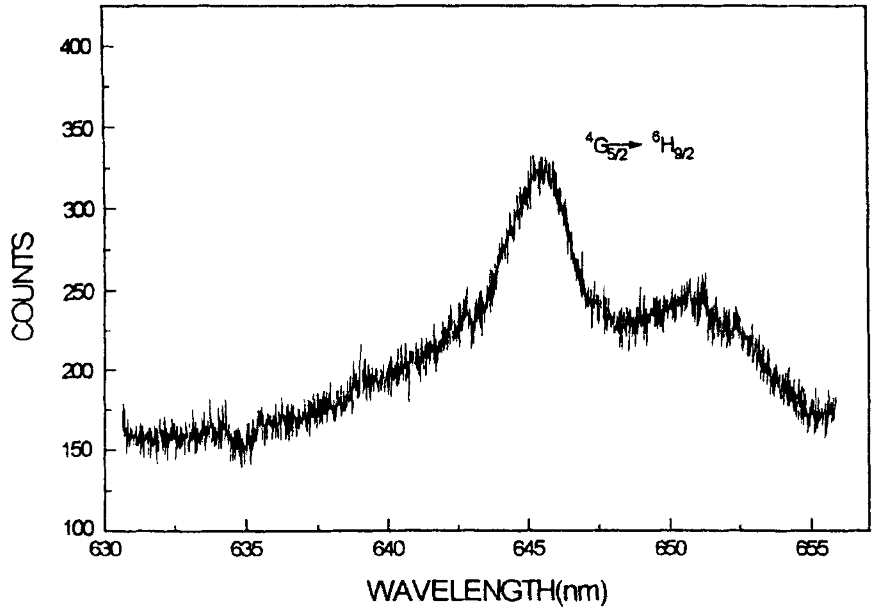

FIGURE 5 The triboluminescence spectrum of **2** at room temperature.

centrosymmetric triboluminescent materials cast doubt on that assumption. Consequently several mechanisms other than piezoelectricity have been proposed to generate the charge separation necessary for triboluminescence in centrosymmetric structures. The importance of trace dopants in determining triboluminescent activity was proven for saccharin [3b]. In discussion of the relation of structure and triboluminescence activity, Sweeting suggested that the phenylring and cation disorder in triethylammonium tetrakis(dibenzoylmethanato)europate may provide a sufficient source of localized polarity to produce the observed activity [2a].

The complex **1** is centrosymmetric but **2** is noncentrosymmetric. From our experiment we conclude that the triboluminescence of **1** and **2** is clearly not dependent on impurities. The observed triboluminescence activity of **2** may be sufficiently explained according to piezoelectric role. Even though the cation (C40) displays disorder from its thermal parameters, its triboluminescent activity also seems to abide by Sweeting's theory. For centric **1**, disorders of all S atoms, all CF_3 groups and the cation exist. According to Sweeting's theory the triboluminescent activity of **1** may be explained with the disorders. However, it is worth noting that **4** [12] is also centrosymmetric (*C*2/*c*) and there are also disorders found in both independent thienyl rings but without triboluminescence. The disorders of

1 are more serious than those of **4**. We compared with europium complexes since there are no other reports of crystal structures of $Sm(TTA)_4Y$ (Y = monovalent cation). The triboluminescent complex **3** [5] is centrosymmetric($P2_1/n$) and there is disorder of three S atoms of the four crystallographically thienyl rings and three of the four CF_3 groups. Moreover, the complexes 4-methylpyridinium tetrakis(2-thenoyltrifluoroacetonato)europate [15] and *N*-ethylpyridinium tetrakis(2-thenoyltrifluoroacetonato)europate [16] crystallize in the centric space group $P\bar{1}$ and 3,6-di(dimethylamine)-diphenyl-iodonium tetrakis(2-thenoyltrifluoroacetonato)europate [17] crystallizes in the centric space group $P2_1/n$. All of them appear to exhibit no disorder of S and F atoms and exhibit no triboluminescent activity. Accordingly, the disorder of all S atoms and CF_3 groups and the cation in centrosymmetric **1** may provide a sufficient condition for triboluminescence, but the smaller disorder of **4** may not be enough to provide a sufficient source of localized polarity to induce triboluminescene. It is also clear from this study that disorder is not sufficient to induce triboluminescence such that a noncentrosymmetric crystal is not sufficient to induce triboluminescence. We are searching for more materials to confirm the result.

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