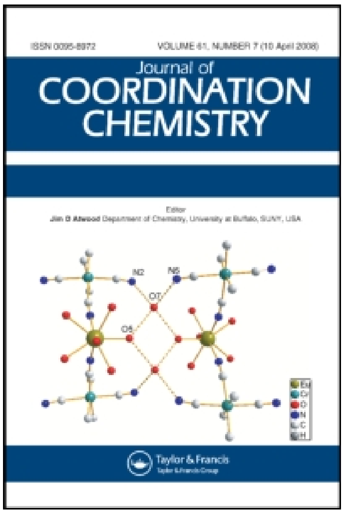

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CRYSTAL STRUCTURE AND TRIBOLUMINESCENCE SPECTRUM OF A CENTROSYMMETRIC LANTHANIDE COMPLEX IMIDAZOLIUM TETRAKIS(DIBENZOYLMETHANATO) EUROPATE

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CRYSTAL STRUCTURE AND TRIBOLUMINESCENCE SPECTRUM OF A CENTROSYMMETRIC LANTHANIDE COMPLEX IMIDAZOLIUM TETRAKIS(DIBENZOYLMETHANATO) EUROPATE

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Triboluminescence of imidazolium tetrakis(dibenzoylmethanato)europate (**1**) was observed. Its crystal structure and the triboluminescent spectrum were determined. The crystal is centrosymmetric and the triboluminscent maximum is similar to that of its photoluminescence. Complex **1** is easily deformable and has weakly bonded interactions between ions and molecules in its lattice; these properties may be responsible for the triboluminescent activity. Complex **1** crystallizes in the orthorhombic space group *Pbcn* with cell parameters $a = 9.844(2)$, $b = 25.701(2)$, $c = 21.171(4)$ Å; $V = 5356(2)$ Å^3 and $Z = 4$. The structure was refined by full-matrix least squares methods to $R = 0.024$ and $R_w = 0.028$.

Keywords: Triboluminescence; photoluminescence; europate complex; ion interaction

INTRODUCTION

Triboluminescence, the emission of light by crystals upon cracking, has been studied for centuries but its causes are still not fully understood. Generally,

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theory predicts that crystals exhibiting triboluminescent activity should have a noncentrosymmetric space group or should be polar and piezoelectric; such materials would certainly generate opposite charge on opposite faces of cracks perpendicular to the polar axis.[1,2] Although evidence for the electrical nature of triboluminescence is quite good, there exist many centrosymmetric crystals which are triboluminescent and many noncentrosymmetric crystals which are not.[3] Consequently, several theories have been raised to explain why crystals having a centrosymmetric space group still exhibit triboluminescent activity.[4–8] Sweeting and Rheingold, respectively, determined the crystal structures of triethylammonium tetrakis(dibenzoylmethanato)europate (**2**)[5] and piperidinium tetrakis(benzoylacetonato) europate (**3**),[8] which have centrosymmetric space groups. They suggested that disorder and ionicity play important roles in triboluminescent activity of centrosymmetric materials. We report here the crystal structure and triboluminescence spectrum of imidazolium tetrakis(dibenzoylmethanato)europate (**1**) which also has a centrosymmetric space group.

EXPERIMENTAL

Preparation of Complex 1

A solution of 1 mmole of anhydrous europium chloride in 20 cm^3 of EtOH was added to a hot solution of 4 mmoles of dibenzoylmethane in 20 cm^3 of EtOH and stirred until the solution became clear and yellow. A solution of excess imidazole (2 mmoles) in 10 cm^3 of EtOH was added to the yellow solution and the mixture was allowed to cool slowly at room temperature and left to stand for a few days when the crude product crystallized. The following procedure is similar to the method reported by Hurt.[9] The crude product was strongly triboluminescent in the dark. Purification by recrystallization was carried out by room temperature evaporation of solvent. Complex **1** has triboluminescent emission with red light in daylight when recrystallized from $CH_3CN-C_2H_5OH$. Found: C, 67.38; H, 4.41; N, 2.61. Calc. for $EuC_{63}H_{49}O_8N_2$(%): C, 67.92; H, 4.40; N, 2.52. The IR of **1** showed peaks at 3353(w), 3025(w), 1598(s), 1553(s), 1516(s), 1479(s), 1458(s), 1409(s), 1310(m), 1286(sh,m), 1220(m), 1183(w), 1068(m), 1023(m), 941(w), 790(m), 757(m), 728(m), 691(m), 613(m), 527(m), 433(m); MP: 178–180°C.

Physical Measurements

Elemental analysis was performed on a Perkin-Elmer 240C instrument. The IR spectrum was recorded on a Nicolet FT-IR 170sx spectrophotometer in

KBr pellets in the range 4000–400 cm^{-1}. Triboluminescence spectra were obtained using an Acton Research Corporation SpectraPro-750, and a Santa Barbara Instruments Group CCD detection system. The grating chosen was blazed for 500 nm. The 10 μm slit used gave a resolution of 0.023 nm. Wavelength accuracy is ±0.1 nm with the 1200 groove per mm grating. A curve was acquired with no crushing and was set as background. The sample was placed as close as possible to the slit in the quartz colorimetric tube and was ground by hand, drawing up small a portion with a glass rod and crushing it against the side of the tube. The photoluminescence spectrum was obtained on an ARC SpectraPro-750, (SBIG) CCD system using an Nd:YAG laser; the 355 nm laser line with a 20 ns pulse width was used to pump the sample.

Crystallography

An orange crystal of dimensions 0.20 × 0.15 × 0.40 mm in a glass capillary was used for data collection at 28°C on a Rigaku AFC7R diffractometer with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω–2θ scans with ω-scan angle $(0.68 + 0.35 \tan\theta)°$ at a scan speed of 8.0° min^{-1} (up to 6 scans for reflection $I < 15\sigma(I)$). Complex **1** crystallizes in the orthorhombic space group *Pbcn* with $a = 9.844(2)$, $b = 25.701(2)$, $c = 21.171(4)$ Å; $V = 5356(2)$ Å^3; $Z = 4$; $D_{\text{calc}} = 1.381$ g cm^{-3}. Unit cell determination was based on 25 reflections in 2θ ranges of 37.4° to 43.1°. Intensity data (in the range of $2\theta_{\max} = 51°$; h: 0–11; k: 0–31; l: −24–0 and 3 standard reflections measured after every 300 reflections showed no decay) were corrected for Lorentz and polarization effects, and empirical absorption corrections based on the ψ-scan of five strong reflections (minimum and maximum transmission factors 0.861 and 1.000). A total of 5319 unique reflections were measured and 2911 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was uniquely determined based on systematic absences and the structure was solved by Patterson methods and expanded by Fourier methods (*PATTY*[10]) and refined by full-matrix least-squares using the software package *TeXsan*[11] on a Silion Graphics Indy computer. One crystallographic asymmetric unit consists of half of the formula unit with Eu(1), C(31) and H(2) atoms at special positions. In the least-squares refinement, all 38 non-H atoms were refined anisotropically; H(1) bonded to N(1), H(2) bonded to C(31) and H(3) bonded to C(32) in the cation were located in the difference Fourier syntheses and their positional parameters were refined; the remaining 22 H atoms of the complex anion at calculated positions with thermal parameters equal to

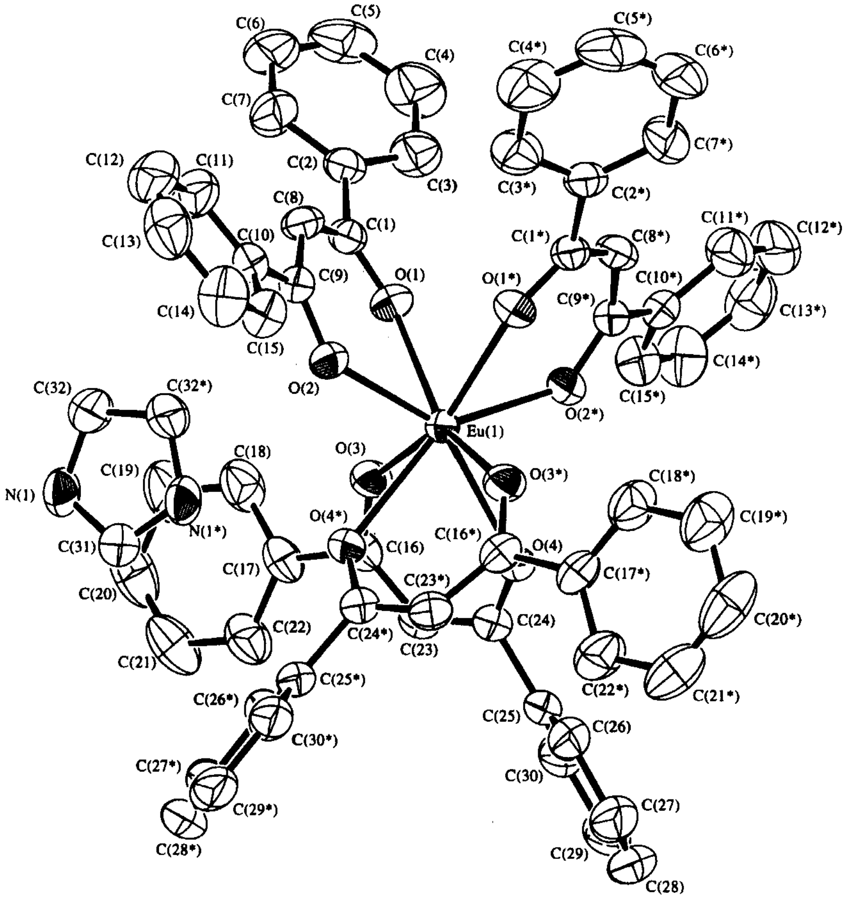

FIGURE 1 An ORTEP drawing of **1**.

1.3 times that of the attached C atoms were not refined. Convergence for 342 variable parameters by least-squares refinement on F with $w = 4F_0^2/\sigma(F_0^2)$, where $\sigma^2(F_0^2) = [\sigma^2(I) + (0.020F_0^2)^2]$ for 2911 reflections with $I > 3\sigma(I)$ was reached at $R = 0.024$ and $R_w = 0.028$ with a goodness-of-fit of 1.35; $(\Delta/\sigma)_{max} = 0.02$. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.23 and 0.43 e Å^{-3}, respectively. An *ORTEP*[12] drawing of the complex anion (Figure 1) shows thermal ellipsoids at the 40% probability level and the numbering scheme. Starred atoms of the complex anion have their coordinates at $-x, y, \frac{1}{2} - z$ and of the cation have their coordinates at $1 - x, y, \frac{1}{2} - z$. Atomic coordinates, and

TABLE I Atomic coordinates and equivalent isotropic thermal parameter for **1**

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Eu(1)	0.0000	0.178473(8)	0.2500	3.247(5)
O(1)	0.1175(2)	0.25103(9)	0.2947(1)	4.10(6)
O(2)	0.1549(2)	0.21011(9)	0.1747(1)	4.03(6)
O(3)	0.1411(2)	0.14553(9)	0.3290(1)	4.39(6)
O(4)	−0.1141(2)	0.10077(9)	0.2968(1)	4.26(6)
N(1)	0.6035(3)	0.1209(1)	0.2646(2)	5.25(9)
C(1)	0.1870(4)	0.2878(1)	0.2721(2)	3.76(9)
C(2)	0.2215(4)	0.3309(1)	0.3175(2)	4.05(9)
C(3)	0.1312(5)	0.3427(2)	0.3650(2)	5.8(1)
C(4)	0.1600(6)	0.3819(2)	0.4082(2)	7.9(2)
C(5)	0.2819(7)	0.4077(2)	0.4048(3)	7.9(2)
C(6)	0.3721(5)	0.3965(2)	0.3584(3)	7.6(2)
C(7)	0.3400(4)	0.3585(2)	0.3149(2)	6.4(1)
C(8)	0.2312(4)	0.2919(1)	0.2096(2)	4.13(10)
C(9)	0.2114(3)	0.2539(1)	0.1639(2)	3.74(9)
C(10)	0.2583(4)	0.2629(1)	0.0980(2)	4.15(9)
C(11)	0.3500(5)	0.3010(2)	0.0815(2)	6.2(1)
C(12)	0.3899(6)	0.3074(2)	0.0189(3)	7.6(2)
C(13)	0.3397(6)	0.2762(2)	−0.0272(2)	7.3(2)
C(14)	0.2477(5)	0.2386(2)	−0.0117(2)	6.9(2)
C(15)	0.2077(4)	0.2319(2)	0.0505(2)	5.5(1)
C(16)	0.1577(4)	0.1028(2)	0.3575(2)	4.27(9)
C(17)	0.2959(4)	0.0941(2)	0.3862(2)	4.7(1)
C(18)	0.3765(5)	0.1369(2)	0.3983(2)	6.1(1)
C(19)	0.5064(5)	0.1302(2)	0.4219(3)	7.9(1)
C(20)	0.5557(5)	0.0809(3)	0.4322(3)	8.3(2)
C(21)	0.4771(5)	0.0386(2)	0.4206(2)	7.6(2)
C(22)	0.3461(5)	0.0450(2)	0.3975(2)	6.2(1)
C(23)	0.0582(5)	0.0643(1)	0.3619(2)	5.0(1)
C(24)	−0.0691(4)	0.0649(1)	0.3319(2)	4.5(1)
C(25)	−0.1562(4)	0.0174(1)	0.3404(3)	5.7(1)
C(26)	−0.2252(5)	−0.0012(2)	0.2893(3)	7.4(1)
C(27)	−0.3037(6)	−0.0465(2)	0.2948(4)	10.9(2)
C(28)	−0.3128(8)	−0.0714(3)	0.3507(6)	13.2(3)
C(29)	−0.2456(7)	−0.0532(2)	0.4028(4)	11.4(3)
C(30)	−0.1649(5)	−0.0086(2)	0.3979(3)	7.9(2)
C(31)	0.5000	0.0914(2)	0.2500	5.4(1)
C(32)	0.5651(4)	0.1708(2)	0.2590(3)	6.4(1)
H(1)	0.679(4)	0.113(1)	0.280(2)	5.5045
H(2)	0.5000	0.058(2)	0.2500	5.5045
H(3)	0.618(4)	0.198(1)	0.268(2)	5.5045
H(4)	0.0487	0.3238	0.3684	6.9618
H(5)	0.0959	0.3908	0.4399	9.4511
H(6)	0.3032	0.4336	0.4352	9.5088
H(7)	0.4562	0.4146	0.3560	9.0829
H(8)	0.4026	0.3514	0.2818	7.6132
H(9)	0.2779	0.3227	0.1975	4.9414
H(10)	0.3862	0.3231	0.1132	7.4346
H(11)	0.4534	0.3340	0.0085	9.0811
H(12)	0.3682	0.2806	−0.0698	8.7365
H(13)	0.2112	0.2169	−0.0438	8.3012
H(14)	0.1440	0.2055	0.0606	6.6170
H(15)	0.3426	0.1709	0.3905	7.3114
H(16)	0.5614	0.1597	0.4309	9.4854

TABLE I (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
H(17)	0.6455	0.0764	0.4478	9.9980
H(18)	0.5114	0.0046	0.4283	9.1225
H(19)	0.2910	0.0154	0.3894	7.4096
H(20)	0.0784	0.0350	0.3875	6.0334
H(21)	−0.2202	0.0165	0.2500	8.8490
H(22)	−0.3506	−0.0597	0.2590	13.0639
H(23)	−0.3667	−0.1019	0.3539	15.8242
H(24)	−0.2537	−0.0708	0.4421	13.6429
H(25)	−0.1165	0.0039	0.4336	9.4925

$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

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

Eu(1)–O(1)	2.389(2)	Eu(1)–O(2)	2.352(2)
Eu(1)–O(3)	2.334(2)	Eu(1)–O(4)	2.496(2)
O(1)–C(1)	1.261(4)	O(2)–C(9)	1.275(4)
O(3)–C(16)	1.265(4)	O(4)–C(24)	1.265(4)
O(1)–Eu(1)–O(2)	71.62(8)		
O(3)–Eu(1)–O(4)	72.13(8)		

bond lengths and angles are given in Tables I and II. Other crystallographic data are available from the authors upon request.

RESULTS AND DISCUSSION

The complex ion is a tetra-bidentate, eight-coordinate Eu(III) complex containing four 1,3-diphenyl-1,3-propanedionato anionic ligands. The eight-coordinate geometry is tetragonal antiprismatic and has an approximate 2-fold rotational axis. The mean of Eu–O bond lengths in **1** (2.393(2) Å) is in accord with those of **2** (2.39(1) Å)[5] and **3** (2.399(5) Å).[8] The bond length range in **1** (2.334–2.496 Å) which is significantly greater than of **2** (2.36–2.41 Å) and **3** (2.36–2.44 Å) reflects the lower symmetry of **1**. O–Eu–O angles within a chelate ring have the following similar averages: **1**, 71.88(8)°; **2**, 70.2(2)°; **3**, 72.1(4)° There is a hydrogen bond observed in the packing diagram of **1** (Figure 2). The imidazole N(1*) proton make a contact of 2.09(4) Å with O(4*) [N(1*)–H···O(4*) = 2.909(4) Å]. The angle of N(1*)–H···O(4*) is 165(4)°. No evidence for disorder in either the cation or anion was resolvable from our data, nor do any of thermal parameters suggest the possibility of disorder masked by thermal activity.

The photoluminescence spectrum of solid **1** in the range 550–720 nm is given in Figure 3. The luminescence is typical of europium centred transitions

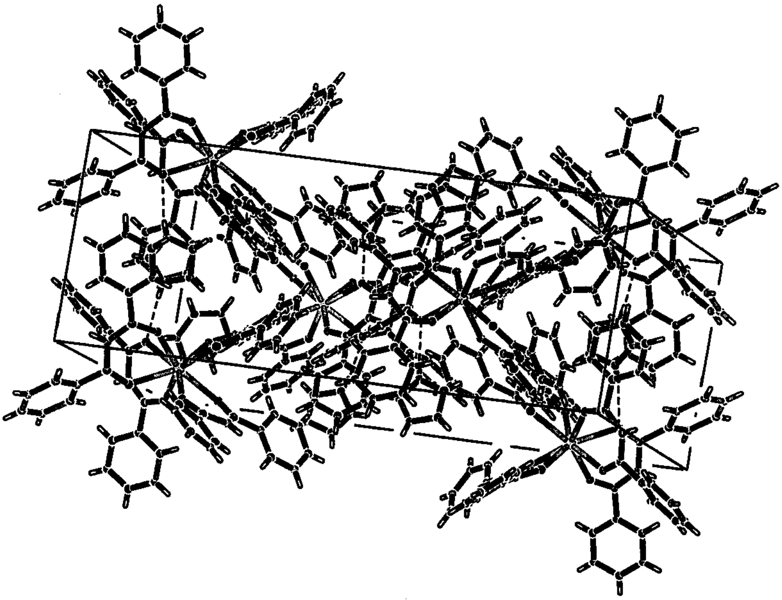

FIGURE 2 Unit cell packing diagram of **1**.

from the $^5D_0$ levels to the lower $^7F_{0-4}$ levels of the ground multiple[13] (data for the very weak $^5D_0 \rightarrow {}^7F_{5,6}$ transitions are difficult to measure) and has been assigned in Table III. The transition from $^5D_0$ to $^7F_0$ has not been observed. In the 32 point groups there are only C_1, C_s, C_n and C_{nv} in which $^5D_0$ to $^7F_0$ transition can be observed. Because complex **1** belongs to the orthorhombic system, the local symmetry of Eu^{3+} may be D_2 or D_{2h} after it is excited.[14] The electric diploe transition $^5D_0 \rightarrow {}^7F_2$ is more intense than the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ reflecting the low site symmetry of the Eu(III) ion. The weak band at 632.05 nm is a result of the vibrational transition spectrum according to the IR spectrum of comoplex **1** (1409 cm^{-1}). The triboluminescence spectrum of **1** is given in Figure 4 and there is no detectable dinitrogen emission. Triboluminescene emission is weaker than that of photoluminescence so we only observed a part of the emission in the range 550–720 nm, corresponding to the most intense photoluminescence. Other characteristic Eu^{3+} ion emission is much weaker than that of the most intense emission. Rheingold[8] stated that the most visible component of the triboluminescent emission of lanthanide complexes is the characteristic photoluminescence of the metallic element. We think part of the emission in the triboluminescence spectrum is centred on the transition of europium from $^5D_0$ to $^7F_2$ levels. The maximum and the splitting of the

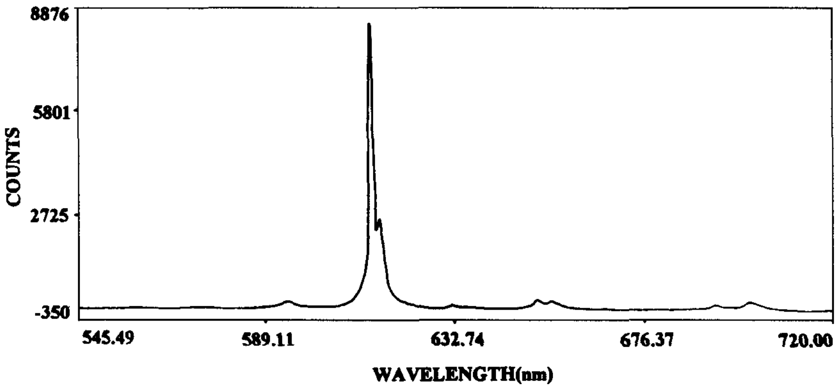

FIGURE 3 Photoluminescence spectrum of solid **1** at room temperature ($\lambda_{ex} = 355$ nm).

TABLE III Spectroscopic data for **1**

Photoluminescence		*Triboluminescence*	
λ (nm)	*Assignment*	λ (nm)	*Assignment*
594.04	$^5D_0 \rightarrow {}^7F_1$		
613.03	$^5D_0 \rightarrow {}^7F_2$	612.95	$^5D_0 \rightarrow {}^7F_2$
615.08	$^5D_0 \rightarrow {}^7F_2$	615.30	$^5D_0 \rightarrow {}^7F_2$
632.05	vibr*		
649.98	$^5D_0 \rightarrow {}^7F_3$		
652.06	$^5D_0 \rightarrow {}^7F_3$		
693.07	$^5D_0 \rightarrow {}^7F_4$		
700.54	$^5D_0 \rightarrow {}^7F_4$		

*Vibr: electronic–vibrational transition.

triboluminescence spectrum of **1** are very similar to that of photoluminescence. For this reason, 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. It has been suggested that a necessary and sufficient condition for charge separation is piezoelectricity of the material. A noncentric space group is necessary for macroscopic piezoelectricity. From evidence derivable from our crystallographic data, complex **1** (which is centrosymmetric) offers no obvious structural basis for triboluminescent activity. If charge separation is necessary for triboluminescence it must be possible to separate charge upon cracking by some means other than piezoelectricity. Sweeting[5] suggested that phenylring and cation disorder in **2** provided a sufficient source of localized polarity to

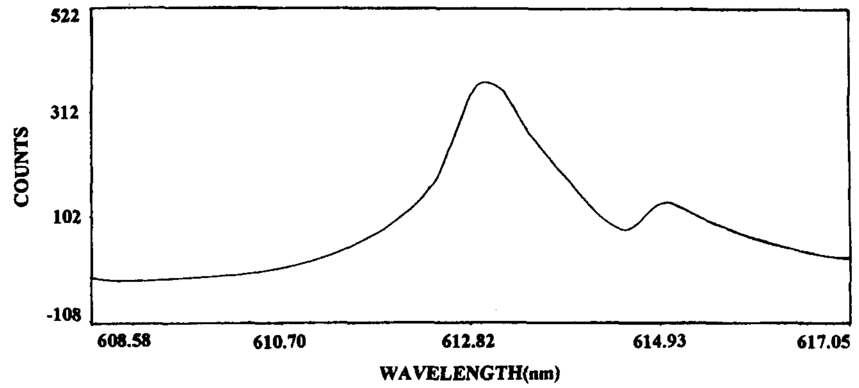

FIGURE 4 Triboluminescence spectrum of 1 at room temperature.

produce the observed activity. A similar situation is not evident in **1**. The importance of trace dopants in determining triboluminescent activity was proven for saccharin.[4] Since **1** was recrystallized from the crude product which was triboluminescent in the dark, impurities cannot be responsible for the triboluminescence of **1**. In a series of triboluminescent anthracyl alcohols, the role of hydrogen bonding was discussed.[1] N–H· · ·O interionic contacts in triboluminescent **2** and **3** were 2.82 Å and 2.84 Å respectively. N–H· · ·O contacts in **2**, whose lattice contained cocrystallized CH_2Cl_2 was 2.86 Å and **2** exhibits no triboluminescence.[5] The question of the role hydrogen bonding plays in triboluminescent activity is a curious one, but it may be provide a location for a pressure-induced deformation of a centric lattice along natural cleavage planes. Rheingold[8] suggested that a centrosymmetric, actively triboluminescent complex is likely to obtain the polar characteristics (local piezoelectricity) essential to its activity from several sources, having in common weak interionic interactions capable of deformation on application of pressure. Complex **1** is a ionic solid that can cleave along intrinsically charged planes, allowing nonpiezoelectric surface-charging pathways. The existence of such planes may be sufficient to explain the observation of activity in centric materials. While the bulk of the crystal relaxes to its original centrosymmetric form,[15] the charged surfaces discharge and excite, *via* photoluminescent emission. Thus the triboluminescence maximum of **1** is very similar to that of the photoluminescence. We are currently searching for other materials to confirm the hypothesis of Rheingold.

Acknowledgments

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