provide the most readily accessible and heuristically useful introduction that is presently available for understanding the fundamental concepts of magnetic coupling phenomena.

Acknowledgment. This work was supported by the National Science Foundation (CHE 80 26812, CHE 85 19913 to C.A.R.) and the National Institutes of Health (HL 15627 to W.R.S.). The Squid susceptometer used in this work was purchased with assistance from an NSF Instrumentation Grant (CHE 82 11349).

Supplementary Material Available: Table IS, anisotropic temperature factors; Table IIS, fixed hydrogen atom positions; Table IIIS, bond distances; Table IVS, bond angles; listings of magnetic susceptibility data for $[Cu(TMP^{\bullet})][SbCl_6]\cdot C_6H_5F$ and $[VO(TPP^{\bullet})][SbCl_6]$ (9 pages); listings (×10) of the observed and calculated structure amplitudes of $[Cu(TPP^{\bullet})][SbCl_6]$ (13 pages). Ordering information is given on any current masthead page.

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Crystal Disorder and Triboluminescence: Triethylammonium Tetrakis(dibenzoylmethanato)europate

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Received September 30, 1986

Abstract: Triethylammonium tetrakis(dibenzoylmethanato)europate is found to exist in two crystal modifications, one of which is triboluminescent (**1**). Both forms crystallize in the centrosymmetric monoclinic space group $I2/a$. The non-triboluminescent form (**2**) contains cocrystallized solvent (CH_2Cl_2); the triboluminescent form does not, but it is disordered. **1**: $a = 25.431$ (4) Å, $b = 9.154$ (2) Å, $c = 27.643$ (4) Å, $\beta = 112.20$ (1)°, $V = 5937$ (2) Å^3, $Z = 4$, $R_F = 7.49\%$. **2**: $a = 25.418$ (8) Å, $b = 17.997$ (7) Å, $c = 27.253$ (8) Å, $\beta = 94.25$ (2)°, $V = 12432$ (6) Å^3, $Z = 8$, $R_F = 5.07\%$. Crystal forms **1** and **2** have the same fluorescence spectra in the solid state, indicating that the dichloromethane does not quench the triboluminescence by quenching the fluorescence. We conclude that the disorder in **1** provides a means of separating charge during fracture and propose a general theory of triboluminescence dependent on charge separation and dielectric breakdown.

Many crystals emit light upon fracture; this phenomenon, known as triboluminescence,[1] has been studied for centuries[2] but is not well understood. There is substantial evidence that charge separation created during fracture is the immediate precursor of the triboluminescent emission.[3] Crystals of nonfluorescent compounds emit the dinitrogen discharge spectrum as their triboluminescence; crystals of fluorescent compounds emit their fluorescence spectra, often modified and occasionally combined with the dinitrogen discharge spectrum, when they triboluminesce. In those cases where the dinitrogen spectrum is observed, it is probable that charge is separated during stress or fracture and recombination occurs by dielectric breakdown of the atmosphere.[4] The emission of the dinitrogen excited during the breakdown (lightning) excites the fluorescence of the crystal. For fluorescent materials which do not exhibit the dinitrogen spectrum, the process may be the same but with a very low intensity of dinitrogen emission. Alternatively, a fluorescent material may be excited directly, with any dinitrogen emission representing an independent phenomenon; spectroscopic studies have not been able to distinguish these two possibilities.[5]

Since triboluminescence is very common among polar crystals, it has often been claimed[6] that noncentrosymmetric, polar, and therefore piezoelectric crystals are *necessary* for the observation of triboluminescence; such materials would certainly generate opposite charge on opposing faces of cracks perpendicular to the polar axis. Although the evidence for the electrical nature of triboluminescence is quite good, there are many centrosymmetric crystals which are triboluminescent[6] and many noncentrosymmetric crystals which are not.[7] Several materials (e.g., saccharin[8] and zinc sulfide[9]) are triboluminescent because of impurities; however, there is no evidence that triboluminescent materials are generally more or less pure than similar nontriboluminescent materials.

We have been searching for a clear pattern of triboluminescence activity as a function of crystal structure that would permit the construction of a predictive theory of triboluminescence. To this end we have studied triethylammonium tetrakis(dibenzoylmethanato)europate, one of the most brilliantly triboluminescent compounds known.[10] In this paper, we compare a triboluminescent crystal form (**1**) with a nontriboluminescent form containing solvent of crystallization (**2**) and provide evidence for a general theory of triboluminescence.

Experimental Section

Preparation and Characterization. The triethylammonium tetrakis(dibenzoylmethanato)europate was synthesized by the method of Hurt et al.;[10] the crude material was strongly triboluminescent. Purification by recrystallization was accomplished by room temperature evaporation of solvent. Form **1** was obtained by recrystallization from methanol (Fisher reagent): yellow plates, strongly triboluminescent, mp 171–80 °C, IR 1600 cm^{-1} (C=O), solid fluorescence max 614 nm (doublet).

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Table I. Crystal and Data Collection Parameters

	triboluminescent 1	non-triboluminescent 2
formula	$C_{66}H_{60}EuNO_8$	$C_{67}H_{62}Cl_2NO_8$
crystal system	monoclinic	
space group	$I2/a$	
a, Å	25.341 (4)	25.418 (8)
b, Å	9.154 (2)	17.997 (7)
c, Å	27.643 (4)	27.253 (8)
β, deg	112.20 (1)	94.25 (2)
V, Å^3	5937 (2)	12432 (6)
Z	4	8
μ(Mo Kα), cm^{-1}	11.0	11.5
D(calcd), g cm^{-3}	1.28	1.32
diffractometer	Nicolet R3	
radiation	Mo Kα (λ = 0.71073 Å)	
temp, K	295	
crystal color	pale yellow	
crystal dimens (mm)	0.18 × 0.32 × 0.40	0.31 × 0.33 × 0.39
reflcns collected	5696	7715
unique reflcns	5218	7411
unique reflcns, $F_o \geq 5\sigma(F_o)$	3733	4197
scan method	omega	Wyckoff
scan range, deg	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 45$
scan speed, deg min^{-1}	var 4–20	var 5–20
standard reflcns	3 standards/97 reflections	
decay, %	2.5	6.1
data/parameter	15.4	7.0
R(*F*), %	7.49	5.07
R(*wF*), %	8.17	5.02
GOF	1.26	1.28
g ($w^{-1} = \sigma^2(F_o) + gF_o^2$)	0.006	0.008
highest peak, final diff map, eÅ^{-3}	1.2 (in Et_3NH^+)	0.9 (1.1 Å from Eu)
Δ/σ	0.12	0.14

Form **2** was obtained by recrystallization from dichloromethane (Fisher reagent): yellow tablets, not triboluminescent, mp 174–80 °C, IR 1600 cm^{-1} (C=O), solid fluorescence max 614 nm (doublet). The fluorescence spectra of **1** and **2** and the triboluminescene spectrum of **1** were indistinguishable from that previously reported.[11,12] Triboluminescence of **1** was excited by grinding the crystals with a glass rod or steel spatula or by shaking a closed vial of crystals. Triboluminescence was examined under low pressure or sulfur hexafluoride (Matheson, 99.99%) on a Schlenck apparatus with use of a flask with a flexible rubber connector to hold the glass rod. Anal. Calcd for $C_{66}H_{60}EuNO_8$: C, 69.10; H, 5.27; Eu, 13.25. Found (one month after preparation) for **1**: C, 69.46; H, 5.21; Eu, 12.69. Found (one month after preparation) for **2**: C, 68.47; H, 4.92; Eu, 12.59. The physical data suggest that **2** contains dichloromethane of crystallization which is readily lost to give a material indistinguishable from **1** (calcd for $C_{66}H_{60}EuNO_8{\cdot}CH_2Cl_2$: C, 65.31; H, 5.04; Eu, 12.35). Infrared spectra were obtained on a Perkin-Elmer 598 (KBr pellet), fluorescence spectra on a Perkin-Elmer MPF-4, and triboluminescence spectra on a Jobin-Yvon 0.1-m spectrometer with use of an EG&G PARC Model 1420 OMA II with a Redicon intensified diode array detector.[12]

Crystallographic Structure Determinations. Care was taken to mount the crystal of **2** wet with solvent and seal it to prevent evaporation of solvent of crystallization during data collection; there was no evidence of solvent incorporation into **1**.

For both **1** and **2**, systematic absences defined the monoclinic space groups *Cc* or *C*2/*c*; this setting was transformed to the nonstandard alternatives *Ia* or *I*2/*a* to take advantage of less obtuse β angles. For **1**, despite *E* statistics suggesting a noncentrosymmetric distribution, fatal correlation problems evidenced by extreme divergencies in temperature factors for atoms symmetry-related in *I*2/*a* proved the *Ia* alternative incorrect. For both **1** and **2**, the centrosymmetric alternatives provided chemically reasonable structures and well-behaved refinements. The unit-cell parameters were derived from the best fit of the angular settings of 25 reflections, $22° \leq 2\theta \leq 28°$. Corrections for linear decay and absorption (empirical, ψ-scan, six-parameter ellipsoids; max/min transmission, **1** = 0.82/0.70, **2** = 0.96/0.91) were applied to the intensity data. Table I provides other details of crystal parameters, data collection, and refinement.

Solution and Refinement for 1. Heavy-atom methods located the Eu atom which was used in a series of difference Fourier syntheses to locate the remaining non-hydrogen atoms. Three of the four unique phenyl rings (the 1×, 3×, and 4× series) are disordered over two sites in approximately 50/50 occupancies (refined occupancy values: 1×, 45/55; 3×, 51/49; 4×, 45/55) and were normalized to 50/50 occupancies. Similarly the Et_3NH^+ ion occupies two sites related by a twofold crystallographic axis through Eu and C(d), an ethyl group β-carbon atom. The occupancies for the Et_3NH^+ atoms were fixed at 0.5.

The final refinement included anisotropic temperature factors for all non-hydrogen atoms except for those of the phenyl rings. Hydrogen atoms were idealized (d(C–H) = 0.96 Å) as isotropic, updated (but unrefined) contributions. The phenyl rings were constrained to rigid, planar hexagonal symmetry (d(C–C) = 1.395 Å).

Solution and Refinement for 2. The Eu atom was located by direct methods and the remaining non-hydrogen atoms from difference Fourier syntheses. Solvent molecules (CH_2Cl_2) were found in two sites: one is a general site which was refined at full occupancy, and the other is a disordered site with both Cl atoms residing on a crystallographic twofold rotational axis. The disordered site was refined with a fixed site occupancy of 0.25 for Cl and C atoms; the occupancy was suggested by difference map electron densities and supported by refined thermal parameters comparable to those for the full occupancy site. All non-hydrogen atoms, except for the C atoms of the solvent molecules, were refined anisotropically; hydrogen atoms and phenyl rings were treated as in **1**.

Tables II and III provide the atomic coordinates for **1** and **2**, respectively, and Table IV lists selected bond distances and angles. Additional crystallographic data are available as supplementary material.

Results

Two crystal forms of triethylammonium tetrakis(dibenzoylmethanato)europate were found in this work, triboluminescent **1** from methanol and nontriboluminescent **2** from dichloromethane. Fresh crystals of **2** contain labile solvent of crystallization. The tablets of **2** are initially transparent, but they quickly develop cracks parallel to their long axis and oblique to their wide face; after several of these cracks develop the crystals shatter perpendicular to the long axis. After an hour of exposure to air, the crystals become completely opaque and can no longer be examined by transmission of light. **2** acquires weak triboluminescence activity if it is heated for 18 h at 50 °C or left at room temperature in a closed container for several months, presumably because of partial conversion of **2** into **1**. This facile loss of solvent accounts for the fact that the infrared spectra, melting points, and elemental analyses of the two forms become indistinguishable—the sample preparation (grinding, heating, shipping) provided an opportunity for loss of solvent from **2**. Dissolution of **2** in methanol and subsequent recrystallization yields strongly triboluminescent crystals with a triboluminescence spectrum indistinguishable from that of **1**. The triboluminescence of **1** is independent of time, but smaller crystals appear to emit less light (this phenomenon is observed for other triboluminescent materials and is probably due to the mechanical difficulty of fracturing the particles when they are below a certain size[13]). The triboluminescence of **1**, as detected by the human eye, is the same when the atmosphere over the crystals is air at 100 kPa or at 0.1–0.5 kPa, or sulfur hexafluoride at 100 kPa.[14]

Dichloromethane is an efficient fluorescence quencher when used as a solvent,[15] and its presence could potentially quench the triboluminescence of **2** via fluorescence quenching. However, **2** is strongly fluorescent, even when examined while still transparent and damp with dichloromethane; its solid state fluorescence spectrum is indistinguishable from that of **1** (whose fluorescence spectrum is indistinguishable from its triboluminescence spectrum[11,12]). Triboluminescent **1** is no longer triboluminescent if broken under liquid dichloromethane; its triboluminescence is also

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	*U*
Eu	2500	2138 (1)	0	50 (1)[a]
O(1)	2476 (3)	749 (9)	714 (3)	73 (3)[a]
O(2)	1664 (3)	621 (9)	-281 (3)	72 (3)[a]
O(3)	1807 (3)	3444 (11)	-702 (3)	82 (3)[a]
O(4)	1950 (3)	3636 (10)	325 (3)	75 (3)[a]
C(1)	1456 (5)	4160 (16)	151 (5)	88 (5)[a]
C(2)	1129 (5)	4330 (18)	-400 (5)	96 (6)[a]
C(3)	1330 (5)	3943 (15)	-777 (5)	87 (5)[a]
C(4)	1348 (5)	162 (15)	-50 (5)	78 (5)[a]
C(5)	1535 (7)	34 (27)	487 (6)	145 (10)[a]
C(6)	2067 (7)	326 (22)	839 (5)	120 (8)[a]
C(1A)	1360 (6)	4323 (14)	964 (5)	63 (5)
C(1B)	1136	4884	1313	82 (7)
C(1C)	769	6077	1172	81 (7)
C(1D)	626	6710	682	95 (8)
C(1E)	850	6149	332	73 (6)
C(1F)	1217	4956	474	50 (4)
C(1G)	1614 (7)	4379 (25)	1150 (8)	132 (12)
C(1H)	1472	5047	1536	160 (16)
C(1I)	941	5701	1407	162 (16)
C(1J)	551	5687	893	100 (8)
C(1K)	693	5019	507	84 (7)
C(1L)	1225	4365	635	73 (6)
C(2A)	477 (7)	5077 (17)	-1439 (6)	151 (7)
C(2B)	139	5382	-1957	237 (14)
C(2C)	258	4727	-2358	185 (10)
C(2D)	715	3767	-2242	195 (11)
C(2E)	1053	3462	-1724	140 (7)
C(2F)	934	4117	-1323	122 (5)
C(3A)	493 (5)	295 (13)	-803 (5)	74 (7)
C(3B)	-52	-157	-1123	77 (7)
C(3C)	-289	-1397	-995	71 (6)
C(3D)	19	-2185	-546	74 (6)
C(3E)	563	-1734	-226	79 (7)
C(3F)	800	-494	-354	38 (4)
C(3G)	266 (7)	-342 (20)	-311 (6)	77 (6)
C(3H)	-231	-1010	-647	98 (8)
C(3I)	-268	-1500	-1134	157 (14)
C(3J)	192	-1322	-1287	134 (12)
C(3K)	689	-654	-952	163 (16)
C(3L)	726	-164	-464	123 (10)
C(4A)	2484 (7)	1781 (19)	1679 (7)	98 (8)
C(4B)	2560	2035	2197	131 (12)
C(4C)	2220	1315	2414	136 (11)
C(4D)	1803	341	2114	144 (13)
C(4E)	1727	87	1596	84 (6)
C(4F)	2068	807	1378	77 (6)
C(4G)	1982 (8)	-751 (33)	1641 (11)	134 (14)
C(4H)	2182	-1153	2165	205 (26)
C(4I)	2766	-1198	2457	175 (20)
C(4J)	3149	-842	2225	141 (15)
C(4K)	2949	-441	1701	118 (12)
C(4L)	2365	-396	1409	78 (7)
N(1)	2929 (7)	-2069 (19)	849 (7)	77 (9)[a]
Ca	3539 (9)	-1806 (32)	1240 (12)	93 (14)[a]
Cb	3650 (16)	-992 (47)	1680 (19)	193 (25)[a]
Cc	2845 (15)	-2936 (26)	348 (12)	106 (18)[a]
Cd	2500	-2726 (45)	0	107 (28)[a]
Ce	2543 (11)	-2647 (29)	1119 (12)	85 (12)[a]
Cf	2771 (13)	-4106 (29)	1417 (11)	89 (12)[a]

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

quenched under hexane, ethanol, and water. Removal of the solvents restored triboluminescence activity in every case.

We determined the crystal structures of the two forms, using **2** that was fresh from and in contact with methylene chloride. The structure and labeling schemes of the cations of **1** and **2** are shown in Figures 1 and 2, respectively. Both are tetra-bidentate, eight-coordinate Eu(III) complexes containing four 1,3-diphenyl-1,3-propanedionato anionic ligands. Both theoretical and empirical aspects of the structures of 8-coordinate complexes have recently been analyzed and reviewed.[16,17] The known eight-coordinate rare-earth propanedionato complexes[18,19] have structures intermediate between dodecahedral (*D*) and square-antiprismatic (*SA*) geometries, and these reviewers have proposed criteria for determining which of these extremes a complex more nearly approximates. *D* symmetry is characterized by the presence of two orthogonal trapezoids[20] and *SA* symmetry by two parallel, staggered squares. Figure 3 depicts the Eu coordination geometry

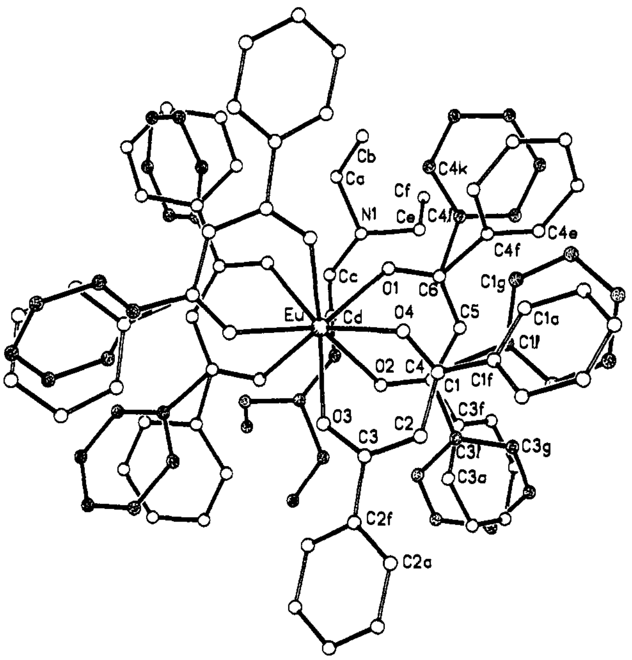

Figure 1. Molecular structure and labeling scheme for **1**. The disorder (see text) in the 1X, 3X, and 4X phenyl rings and Et_3NH^+ ion are depicted by open and stippled atoms (either set is independently occupied). The phenyl ring carbon atoms are labeled in alphabetical order in the sequence indicated by the two labels shown.

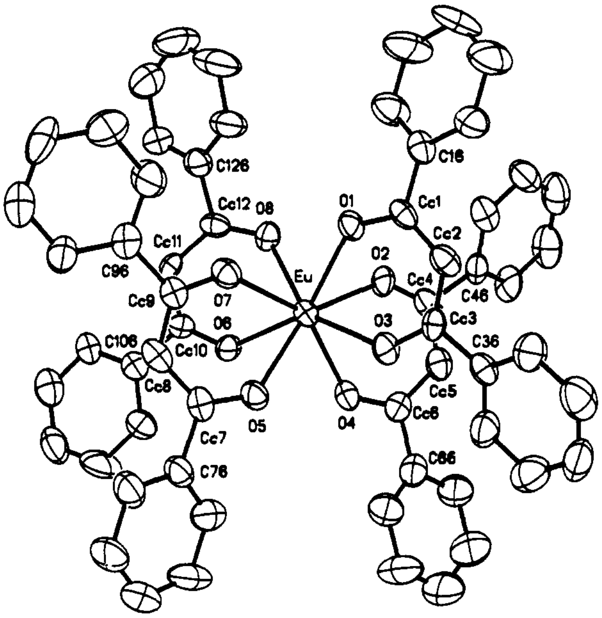

Figure 2. Molecular structure and labeling scheme for the anion of **2** (only the ipso carbon atoms are labeled for clarity). Thermal elipsoids are drawn at the 40% probability level.

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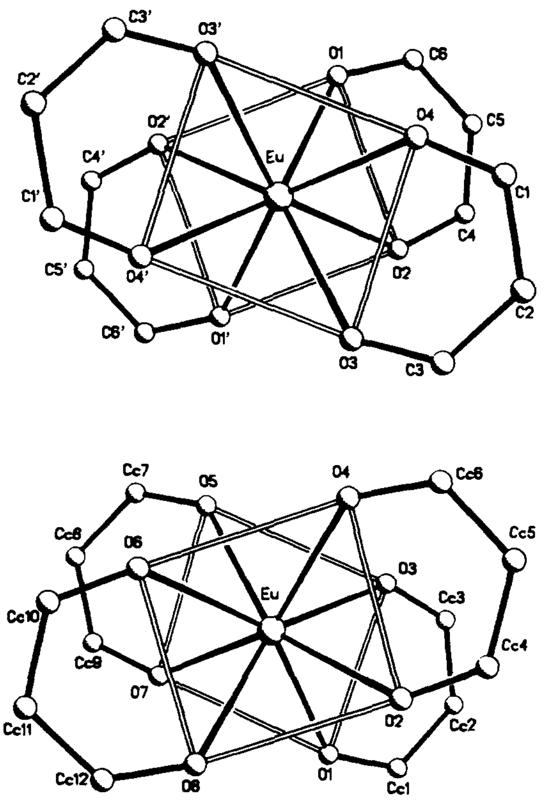

Figure 3. The approximate antiprismatic coordination geometries for **1** (upper) and **2**. The open lines are construction lines.

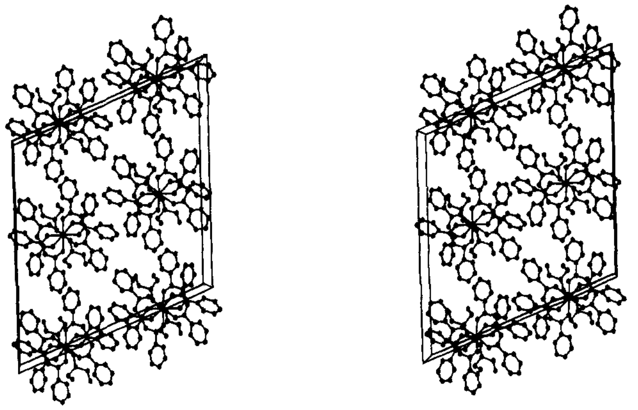

Figure 4. Unit cell packing diagram for **1** as viewed along the *b* axis (*c* vertical). One of the two sets of disordered phenyl rings is depicted (Et_3NH^+ is shown in both sites).

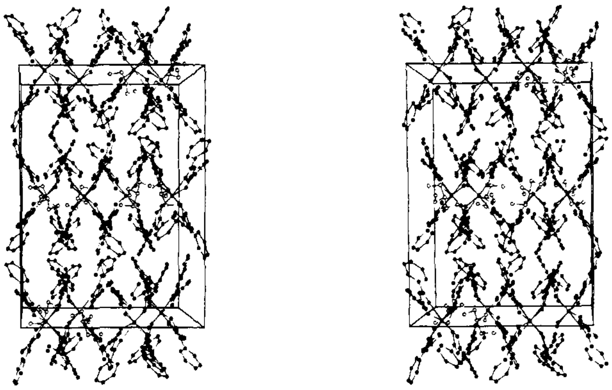

Figure 5. Unit cell packing diagram for **2** as viewed along the *c* axis (*a* vertical). The cations are shown with open circles. Solvent molecules have been deleted for clarity.

for both **1** and **2** and contains O⋯O vectors which reveal a reasonable approximation to *SA* symmetry; Filipescu et al.[21] concluded that the symmetry of **1** was *SA* from the visible spectrum. Alternatively, *D* symmetry could have been depicted by trapezoid construction with use of the sets [O(1), (O(2), O(4′), O(3′)] and [O(1′), O(2′), O(4), O(3)] for **1** and [O(1), O(3), O(6), O(8)] and [O(2), O(4), O(5), O(7)] for **2**. Two straightforward means of assessing the relative closeness of each structure to *D* and *SA* extremes are to (1) compare the average deviations of the O atoms from the planes and trapezoids characterizing each symmetry and (2) to compare the angle made by the intersection of these planes. The average deviation of the O atoms from the squares for **1** is 0.06 Å, for **2**, 0.09 Å; the average deviation from the trapezoids for **1** is 0.24 Å, for **2**, 0.18 Å. For *SA* symmetry the planes must be parallel; for **1**, the interplanar angle is defined by the crystallographic symmetry as 0°, and for **2**, the measured angle is 1.9 (5)°. The intertrapezoidal angle for both **1** and **2** is 85 (1)°, compared to the ideal values of 90° for *D* symmetry and 77.4° for *SA* symmetry.[16] Thus, the stereochemistries of **1** and **2** deviate significantly from both *SA* and *D* geometries, but they more closely resemble (from the average deviations) the *SA* ideal.[22]

Three of the four crystallographically unique phenyl rings in **1** display approximately equally occupied alternative positions correlated to equivalently occupied alternative positions for the Et_3NH^+ ion as shown in Figures 1 and 4 (see Experimental Section for details). With the exception of the minor occupancy site for a solvent molecule (CH_2Cl_2), no disorder is found in **2**. The chelate rings in both structures are folded along the O⋯O vectors (Figure 5) to produce dihedral angles which range from 19.0 to 25.6° (av 22.3°) for **1** and from 14.8 to 35.0° (av 25.7°) for **2**. These angles may be compared to the averages obtained by Il'inskii[19] for the diethylammonium **3a** (21.5°) and the pyridinium **3b** (20.9°) salts of tetrakis(benzoylacetonato)europate and by Burns[18] for cesium tetrakis(hexafluoroacetylacetonato)europate (**4**) (8.0°). From these limited data, the folding angle would appear correlated to steric effects within the anions, and not anion–cation or anion–solvent contacts. The broad range of values found for **1** and **2** represent varying balances in the compromise between O⋯O repulsions and phenyl ring interactions.

In all of the complexes, **1**–**4**, the two Eu–O distances in each chelate ring show a pattern of a 0.02–0.04-Å difference, but all complexes have the same average Eu–O distance, 2.39 Å. The O–Eu–O angles within a chelate ring have the following similar averages: **1**, 70.2 (2)°; **2**, 72.0 (3)°; **3a**, 70.3 (10)°; **3b**, 72.1 (4)°; and **4**, 72.5 (8)°. A "normalized bite", *b*, defined as the ratio of the O⋯O to Eu–O distance,[17] may be computed: **1**, 1.16; **2**, 1.15; **3a**, 1.15; **3b**, 1.18; and **4**, 1.18.[18] The value of *b* has been correlated to stereochemistry:[17] as *b* increases, the stereochemistry tends more to *SA* geometry. The values of *b* for **1**–**4** characterize intermediate character verging on the *SA* extreme, in agreement with the conclusion from deviations from the characteristic planes.

A neutral adduct description, $HEuL_4.NR_3$, for **3a**, rather than the ammonium europate composition we describe for **1** and **2** has been claimed.[19] The neutral structure is based on circumstantial evidence, largely the failure to locate crystallographically any of the atoms of the diethylammonium ion and the assumption that Et_2NH molecules, and not $Et_2NH_2^+$ ions, were disordered in channels in the crystal lattice. No evidence for such behavior is seen in either **1** or **2**; definite cation positions have been determined, and the average angles about N in **1**, 114 (2)°, and **2**, 111 (1)°, are more typical of Et_3NH^+ than Et_3N. In the unit-cell packing of structures of **1** (Figure 4), **2** (Figure 5), **3a**, and **3b**,[19] large voids in the lattice are created by the packing of the ligand phenyl rings; these voids are aligned in **3a** to form channels (estimated mean diameter, 5 Å) with proposed Et_2NH occupation. In **1**, **2**, and **3b** these voids are offset and do not form channels; they are apparently not large enough to accommodate CH_2Cl_2 molecules since the unit cell volume per molecule is 5% larger for **2** than for **1**. The CH_2Cl_2 molecules in **2** provide no significant nonbonded

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[21] Filipescu, N.; Degnan, J. J.; McAvoy, N. *J. Chem. Soc. A* **1968**, 1594–1598.

[22] A more appropriate description for these complexes might be "tetragonal antiprismatic" (Il'inskii).

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for **2**

	x	*y*	*z*	*U*
Eu	−14 (1)	3577 (1)	2364 (1)	47 (1)[a]
Cl(1)	266 (2)	1937 (3)	487 (2)	155 (2)[a]
Cl(2)	4625 (2)	9064 (3)	985 (2)	168 (3)[a]
Cl(3)	2500	949 (7)	0	127 (11)[a]
Cl(4)	2500	−590 (14)	0	167 (15)[a]
O(1)	−327 (2)	4275 (4)	3037 (2)	60 (3)[a]
O(2)	−695 (2)	2843 (4)	2676 (2)	61 (3)[a]
O(3)	−709 (2)	4367 (3)	2059 (2)	59 (3)[a]
O(4)	−448 (2)	2912 (4)	1702 (2)	62 (3)[a]
O(5)	375 (2)	4145 (4)	1679 (2)	60 (3)[a]
O(6)	659 (2)	2759 (3)	2104 (2)	57 (3)[a]
O(7)	699 (3)	4344 (4)	2647 (2)	63 (3)[a]
O(8)	392 (2)	2899 (3)	3048 (2)	57 (3)[a]
Cc(1)	−757 (4)	4579 (5)	3113 (4)	53 (4)[a]
Cc(2)	−1135 (4)	4814 (5)	2731 (4)	60 (5)[a]
Hc(2)	−1443	5071	2825	72
Cc(3)	−1091 (3)	4697 (5)	2236 (4)	47 (4)[a]
Cc(4)	−1135 (4)	2659 (5)	2496 (4)	60 (5)[a]
Cc(5)	−1282 (4)	2615 (6)	1982 (4)	68 (5)[a]
Hc(5)	−1642	2497	1880	83
Cc(6)	−924 (4)	2735 (5)	1616 (4)	56 (4)[a]
Cc(7)	822 (4)	4363 (5)	1607 (4)	57 (4)[a]
Cc(8)	1218 (4)	4544 (5)	1979 (4)	64 (5)[a]
Hc(8)	1564	4670	1887	79
Cc(9)	1124 (4)	4549 (5)	2477 (4)	54 (4)[a]
Cc(10)	1112 (4)	2599 (5)	2294 (3)	43 (4)[a]
Cc(11)	1253 (4)	2655 (5)	2806 (3)	58 (4)[a]
Hc(11)	1614	2577	2923	66
Cc(12)	882 (4)	2819 (5)	3145 (3)	57 (4)[a]
C(11)	−590 (3)	4244 (4)	3985 (3)	100 (6)[a]
C(12)	−690	4305	4480	130 (8)[a]
C(13)	−1063	4814	4624	123 (8)[a]
C(14)	−1336	5261	4273	119 (8)[a]
C(15)	−1236	5199	3778	88 (6)[a]
C(16)	−863	4691	3634	61 (4)[a]
C(31)	−1589 (3)	4628 (4)	1422 (4)	80 (5)[a]
C(32)	−1980	4879	1076	99 (7)[a]
C(33)	−2300	5476	1187	100 (7)[a]
C(34)	−2229	5823	1645	104 (7)[a]
C(35)	−1837	5572	1992	88 (6)[a]
C(36)	−1518	4974	1880	58 (4)[a]
C(41)	−1568 (3)	2841 (4)	3256 (3)	77 (5)[a]
C(42)	−1926	2645	3599	93 (6)[a]
C(43)	−2278	2061	3499	110 (8)[a]
C(44)	−2273	1672	3056	109 (7)[a]
C(45)	−1916	1868	2714	89 (5)[a]
C(46)	−1563	2452	2814	63 (5)[a]
C(61)	−1544 (4)	2274 (5)	904 (4)	111 (7)[a]
C(62)	−1719	2297	407	175 (11)[a]
C(63)	−1471	2765	87	213 (15)[a]
C(64)	−1049	3208	264	163 (11)[a]
C(65)	−874	3185	761	98 (6)[a]
C(66)	−1122	2718	1081	77 (5)[a]
C(71)	682 (3)	3987 (5)	729 (4)	101 (6)[a]
C(72)	794	4031	237	162 (10)[a]
C(73)	1174	4531	94	189 (13)[a]
C(74)	1441	4986	444	142 (9)[a]
C(75)	1329	4942	936	90 (6)[a]
C(76)	949	4443	1079	74 (5)[a]
C(91)	2049 (4)	5048 (5)	2740 (3)	84 (6)[a]
C(92)	2412	5331	3101	103 (7)[a]
C(93)	2270	5410	3583	110 (7)[a]
C(94)	1766	5206	3704	142 (9)[a]
C(95)	1403	4923	3342	108 (7)[a]
C(96)	1545	4844	2860	62 (5)[a]
C(101)	1400 (3)	2504 (4)	1450 (3)	81 (5)[a]
C(102)	1750	2276	1109	122 (8)[a]
C(103)	2217	1914	1268	113 (8)[a]
C(104)	2335	1780	1769	90 (6)[a]
C(105)	1985	2009	2110	68 (5)[a]
C(106)	1518	2371	1951	57 (4)[a]
C(121)	822 (3)	3428 (5)	3941 (4)	94 (6)[a]
C(122)	966	3523	4441	138 (9)[a]
C(123)	1372	3095	4669	181 (13)[a]
C(124)	1633	2573	4397	145 (9)[a]
C(125)	1488	2478	3897	94 (6)[a]
C(126)	1082	2906	3670	69 (5)[a]
N(1)	89 (4)	6522 (5)	1710 (3)	67 (4)[a]
C(1)	16 (6)	6136 (7)	2572 (5)	135 (8)[a]
C(2)	269 (6)	6044 (7)	2131 (5)	112 (7)[a]
C(3)	526 (5)	6601 (8)	1372 (6)	111 (7)[a]
C(4)	389 (7)	7147 (9)	962 (6)	151 (10)[a]
C(5)	−405 (5)	6258 (7)	1439 (5)	89 (6)[a]
C(6)	−365 (4)	5531 (6)	1149 (4)	84 (5)[a]
C(7)	131 (6)	1600 (8)	1070 (5)	119 (5)
C(8)	2655 (27)	182 (11)	279 (22)	147 (25)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

contacts. The anions are chiral; the lattices are racemic mixtures as requied crystallographically.

Discussion

Several mechanisms have been proposed for triboluminescence. It has been suggested that focusing of mechanical energy can excite molecules, but the energy is insufficient to excite fluorescence.[5] Radiationless transitions have been suggested,[23,24] but there is no spectroscopic or other evidence of the molecular distortion required for the transition.[12,24] It is generally accepted that the primary event in triboluminescence is the recombination of charges separated during fracture.[5] We consider the implications of this work with respect to the charge recombination mechanism, beginning with the charge separation and concluding with the mechanism of excitation of the fluorescence.

Charge Separation. It has been asserted[6] that only piezoelectric (noncentrosymmetric) crystals may be triboluminescent because only such crystals can develop opposite charges on the opposing faces of a developing crack. The crystal structures of triboluminescent materials show that a noncentrosymmetric space group is neither necessary nor sufficient for triboluminescence; for example, of 40 triboluminescent aromatic compounds, only 25 crystallize in noncentrosymmetric space groups,[25] and of 10 noncentrosymmetric sugars, only 5 are triboluminescent.[7] The present study again demonstrates that materials which are centrosymmetric can be triboluminescent: **1** crystallizes in *I*2/*a*. One material has been found to be triboluminescent because of tri-

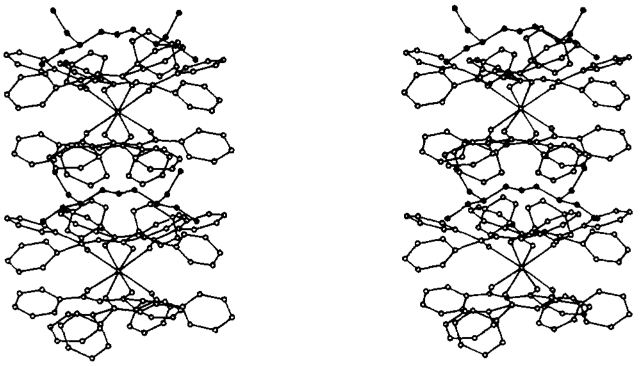

Figure 6. Stereo view of **1** with the crystallographic twofold axis vertical. This view emphasizes the remoteness of the 2× phenyl ring from either of the Et_3NH^+ sites and clearly depicts which of the alternate ring sites for the 1×, 3×, and 4× phenyl rings correlates with which cation site.

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Table IV. Selected Bond Distances and Angles for **1** and **2**

bond type	**1**		**2**	
	A. Bond Distances (Å)			
Eu–O	Eu–O(1)	2.375 (9)	Eu–O(1)	2.405 (6)
	Eu–O(2)	2.409 (7)	Eu–O(2)	2.384 (6)
	Eu–O(3)	2.393 (8)	Eu–O(3)	2.370 (6)
	Eu–O(4)	2.369 (9)	Eu–O(4)	2.368 (6)
			Eu–O(5)	2.405 (6)
	Eu–O(av)	2.39 (1)	Eu–O(6)	2.405 (6)
			Eu–O(7)	2.361 (6)
			Eu–O(8)	2.396 (6)
			Eu–O(av)	2.39 (1)
O–C (av)	1.26 (2)		1.25 (2)	
chain C–C (av)	1.39 (2)		1.41 (2)	
	B. Bond Angles (deg)			
O–Eu–O (intra)	O(1)–Eu–O(2)	70.2 (2)	O(1)–Eu–O(3)	74.2 (2)
	O(3)–Eu–O(4)	70.2 (3)	O(2)–Eu–O(4)	75.1 (2)
			O(5)–Eu–O(7)	69.8 (2)
			O(6)–Eu–O(8)	69.0 (2)
O–Eu–O (inter)	O(1)–Eu–O(4)	77.8 (3)	O(1)–Eu–O(2)	74.2 (2)
	O(1)–Eu–O(3)	134.7 (3)	O(1)–Eu–O(4)	133.1 (2)
	O(1)–Eu–O(8′)	115.1 (4)	O(1)–Eu–O(5)	123.3 (2)
	O(1)–Eu–O(4′)	146.5 (2)	O(1)–Eu–O(6)	145.9 (2)
	O(1)–Eu–O(2′)	73.7 (3)	O(1)–Eu–O(7)	74.7 (2)
	O(1)–Eu–O(3′)	80.4 (3)	O(1)–Eu–O(8)	79.7 (2)
	O(2)–Eu–O(4)	83.3 (3)	O(2)–Eu–O(3)	85.1 (2)
	O(4)–Eu–O(1′)	146.5 (2)	O(2)–Eu–O(5)	149.7 (2)
	O(4)–Eu–O(4′)	109.1 (3)	O(2)–Eu–O(6)	108.5 (2)
	O(4)–Eu–O(2′)	141.9 (2)	O(2)–Eu–O(7)	140.2 (2)
	O(4)–Eu–O(3′)	76.0 (3)	O(2)–Eu–O(8)	74.0 (2)
	O(2)–Eu–O(1′)	73.7 (3)	O(3)–Eu–O(5)	79.1 (2)
	O(2)–Eu–O(4′)	141.9 (2)	O(3)–Eu–O(6)	142.4 (2)
	O(2)–Eu–O(2′)	109.4 (4)	O(3)–Eu–O(7)	107.4 (2)
	O(2)–Eu–O(3′)	147.0 (3)	O(3)–Eu–O(8)	147.8 (2)
	O(3)–Eu–O(1′)	80.4 (3)	O(4)–Eu–O(5)	79.5 (2)
	O(3)–Eu–O(4′)	76.0 (3)	O(4)–Eu–O(6)	76.5 (2)
	O(3)–Eu–O(2′)	147.0 (3)	O(4)–Eu–O(7)	147.8 (2)
	O(3)–Eu–O(3′)	119.9 (4)	O(4)–Eu–O(8)	119.0 (2)
			O(5)–Eu–O(6)	71.8 (2)
			O(5)–Eu–O(7)	69.8 (2)
			O(5)–Eu–O(8)	129.9 (2)
			O(6)–Eu–O(7)	84.7 (2)
			O(6)–Eu–O(8)	69.0 (2)
			O(7)–Eu–O(8)	76.6 (2)
Eu–O–C (av)	134 (1)		133 (1)	
O–C–C (av)	124 (1)		125 (1)	
chain C–C–C (av)	125 (2)		123 (1)	

boluminescent impurities (saccharin is often contaminated with *p*-toluenesulfonamide[26]); some centrosymmetric salts doped with luminescent ions (e.g., zinc sulfide[9]) also exhibit triboluminescence. Since nontriboluminescent **2** was prepared from triboluminescent **1** (which was regenerated from **2**), impurities cannot be responsible for the difference between **1** and **2**. It has also been pointed out that, even in centrosymmetric crystals, cleavage along some planes will not generate reflection symmetry (for example, the 111 plane of sodium chloride[5]). Cleavage between enantiomeric molecules in crystalline racemates might give mirror symmetry, but cleavage between identical molecules could provide the dissymmetry needed for charge separation. In addition, many centrosymmetric crystal structures contain multiple, independent molecules, each of which may have very different crystallographically imposed symmetries. **1** and **2** are both racemic and have similar packing of ions in the crystal.

There are two important differences between the crystal structures of triboluminescent **1** and nontriboluminescent **2** which may illuminate the mechanism of charge separation: **1** is disordered and **2** contains dichloromethane, a potent fluorescence inhibitor. The possibility that **2** is not triboluminescent because the fluorescence is quenched by the dichloromethane in the crystals can be rejected because **2** is strongly fluorescent. The disorder in **1** 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. We believe that the disorder in the triethylammonium ion position is of minor importance to the triboluminescence; the europate complex ion would be a more energetically favorable site for a charge defect of either sign,[27,28] and the emission spectrum is that of the europate ion (changing the cation only shifts the fluorescence spectrum about 1 nm[11]). The crystal structures of the nontri-

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(28) John D. Bartmess, personal communication. In the gas phase, electrons are usually only bound by π systems and are not bound by chlorinated methanes.

boluminescent diethylammonium (**3a**) and piperidinium (**3b**) tetrakis(benzoylacetonato)europate have been determined;[19] the latter has no disorder. The centrosymmetric *B*2/*b* diethylammonium crystals (**3a**) show no disorder in the europate ions, but the diethylammonium ions could not be crystallographically located; however, the material is not triboluminescent. The disorder in the dichloromethane positions in **2** is not expected to permit triboluminescence since its electron affinity and ionization potential make it unlikely that charge of either sign will be accumulated there.[27,28] Thus we conclude that the disorder in the fluorescent europate ion provides the local dissymmetry needed to support charge separation.

All real crystals, of course, are disordered and impure (have X- and Y-traps); both kinds of defect could provide a means for local charge separation. Are all solids, therefore, triboluminescent? Our results and those of others[4,5] indicate that for triboluminescence to occur the voltage developed must be adequate to cause dielectric breakdown in the atmosphere in the crack; only materials able to attain this voltage will be triboluminescent.[29] The resulting discharge could occur between opposing faces of a growing crack or between oppositely charged patches on the same face.

It has been found that salts doped with luminescent ions emit light both during elastic and plastic deformation and upon cleavage.[30] It was proposed that unpinning of dislocations from defects and subsequent impact of moving dislocations on other defects excites the luminescent centers during deformation but that the emission upon cleavage is due to an electric discharge through the atmosphere. Light emission on deformation appears to have a different cause from the emission upon cleavage.[31]

Fluorescence Excitation. Assuming generation of an adequate voltage for dielectric breakdown of the atmosphere, the excitation of the molecules of the crystal could occur by electron bombardment or indirectly by excitation of the fluorescence of the molecules by the dinitrogen emission in the UV–vis. Triboluminescent materials with no photoemission above about 200 nm exhibit only the dinitrogen discharge spectrum. For a few fluorescent materials, the triboluminescence spectrum contains both the dinitrogen discharge and the fluorescence of the compound;[24,32,33] these emissions could be independent events, but their simultaneous presence in the triboluminescence spectrum has generally been interpreted to mean that dinitrogen emission excites the molecules of the crystal. **1**, like most fluorescent compounds, exhibits a triboluminescence spectrum indistinguishable from that of its fluorescence, with no detectable dinitrogen emission.[12] The best available sensitivity for triboluminescence spectra has not detected dinitrogen emission intensity less than 1% that of the fluorescence (e.g., uranyl nitrate hexahydrate[33,34]). With comparison of the signal-to-noise ratios of the triboluminescence spectra[12] of sucrose (the most intense nonfluorescent compound[35]) and **1**, we estimate that the dinitrogen emission contributes less than 0.1% of the total emission of **1**; the dinitrogen emission may be present but too weak to be detected.

The disappearance of triboluminescence when crystals of **1** are crushed under several liquids, and its subsequent recovery upon removal of the liquids suggest that air is necessary for the triboluminescence. The lack of sensitivity of the triboluminescence to the identity of the atmosphere seems contradictory but has been observed by others.[36] The triboluminescence of fluorescent materials has not been previously studied at reduced atmospheric pressure. In nonfluorescent materials such as sucrose, the emission reaches a maximum at about 1 kPa because the breakdown voltage of air is a minimum at that pressure.[37] If the triboluminescence of **1** is excited by the emission of nitrogen in the surrounding atmosphere alone, it too would be expected to show a maximum near 1 kPa; since it does not, an alternate explanation is necessary. Air trapped in the crystals may mask the effect of changing the atmosphere or gaseous fragments of the crystal may facilitate the discharge.[3,4] It is unlikely that the molecules are excited directly by electron bombardment since the electroluminescent spectrum is seldom identical with the fluorescence spectrum.[9,38] The ability of liquid to quench the triboluminescence indicates that the time between crack formation and the emission must be sufficient for the liquid to enter the crack; measurements on single crystals indicate that the time is less than 1 ms.[39] The fluorescence spectra of **1** and **2** are excited optimally at 400 nm, with no excitation by wavelengths longer than 480 nm; the emission maxima are at 614 nm. We conclude that emission by molecules in the surrounding gas between 320 and 480 nm (probably the dinitrogen ${}^3\pi_u \rightarrow {}^3\pi_g$ emission, 280–440 nm), excited by electric discharge upon cleavage of **1**, excites the aromatic rings of the ligand; the ligand transfers excitation to the f-electrons of the europium (the emission is predominantly ${}^5D_0 \rightarrow {}^7F_2$[11]). The emission causing the fluorescence excitation is absorbed very efficiently by the crystal because the gas-filled crack is almost surrounded by a fluorescent material whose excitation spectrum corresponds well to the emission.

Conclusions

For triethylammonium tetrakis(dibenzoylmethanato)europate, disorder in the aromatic rings of crystal form **1** is a sufficient condition to permit charge separation upon cleavage. A voltage is developed across the growing crack adequate to cause a discharge through the surrounding gas. This discharge, confirmed by the disappearance of the triboluminescence under liquids, excites the phenyl rings of the ligands which in turn excite the europium f states. Emission from chelated europium provides the observed triboluminescence. We believe this discovery of the importance of disorder provides a sufficient condition for the triboluminescence of other centrosymmetric crystals and that the triboluminescence of other fluorescent materials is excited by light generated by a gas discharge. We are currently examining other materials to confirm this theory.

Acknowledgment. L.M.S. thanks the Faculty Research Committee of Towson State University for assistance and George M. Whitesides for his hospitality and encouragement during a sabbatical in his laboratory. The diffractometer was purchased in part by a National Science Foundation grant to the University of Delaware. The authors also thank Steven D. Brown, Bruce M. Foxman, and George M. Whitesides for helpful discussions.

Supplementary Material Available: Complete lists of bond lengths and bond angles, anisotropic thermal parameters, and H atom coordinates for **1** and **2** (9 pages); listing of observed and calculated structure factors for **1** and **2** (47 pages). Ordering information is given on any current masthead page.

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(29) Metals are not triboluminescent, presumably because of their inability to maintain charge separation. The development of an adequate voltage may set an upper limit on the conductivity of a triboluminescent material. In the case of **1** and **2**, it is unlikely that a difference in conductivity could account for the difference in triboluminescence activity.

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