Al/Al(III) 1.5:1 melt reference, can be made. Though these potentials are somewhat less positive than that observed experimentally, the estimates are qualitatively reasonable.

In addition to redox potentials, IR stretching frequencies, NMR chemical shifts, and enthalpies of solvation or transfer of various complexes and ions are correlated with donicity.[6] By direct comparison or by analogy, this body of work can be drawn upon in considering the chemistry of various compounds in the melt.

Unfortunately, the DN/AN approach is not universally applicable in the simple way outlined above. An interesting class of cases in which donicity considerations are unlikely to adequately describe chemistry in the melts is that of "soft" ions or compounds intereacting with the melt. Since most solvents have hard reactive sites, donor and acceptor numbers do not adequately reflect the reactivity of soft sites. (Of course, this also means that the consideration of solvent "softness" is not important in many cases.)

No work done to date in ambient-temperature chloroaluminates has specifically considered the influence of softness of ions studied on their chemistry. A situation in which this type of interaction could be important is the solvation of ions such as Cu(I) or Ag(I), which are known to be quite soft. Indeed, it may be possible to observe some preferential solvation effects for these ions in solutions of melts with cosolvents or with soft bases present. Ag(I) is known to be strongly solvated by acetonitrile. Perhaps I^- present in melts would also provide additional stabilization for soft metal ions.

Another type of reaction that is not completely predictable on the basis of DN/AN comparisons is that in which further rearrangement takes place after initial adduct formation. The further rearrangement can provide an additional energetic driving force to the reaction. Consider the case of an alcohol added to the melt. The oxygen on the alcohol will behave as a donor toward Al(III) to form an adduct.[36] This initial step can be followed by loss of a proton into the melt, which solvates the proton. This solvation step can provide an additional driving force.

The scope of the reactions described that are not likely to be readily explicable by DN/AN considerations certainly limits the power of the donor–acceptor approach. However, this approach, for all its crudeness, still can provide at least qualitative information on the reactivity of these melts toward a wide variety of solutes. Furthermore, the determination of the AN and DN values described above represents a first attempt to systematically compare chemistry in a molten salt system with that in typical organic solvents. From this point of view, we know that toward solutes which are not very basic, a basic melt will behave like DMF. On the other hand, acidic melts are similar in acidity to trifluoroacetic acid. This information provides at least a starting point for the interpretation of chemistry observed in the melt and for speculation on the suitability of the melt as a solvent for classes of chemical reactions.

Acknowledgment. We wish to acknowledge helpful discussion with Dr. Marek Lipsztajn. This work was supported in part by the Air Force Office of Scientific Research.

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Crystal Structures of Three Brilliantly Triboluminescent Centrosymmetric Lanthanide Complexes: Piperidinium Tetrakis(benzoylacetonato)europate, Hexakis(antipyrine)terbium Triiodide, and Hexaaquadichloroterbium Chloride

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Received October 27, 1988

The crystal structures of three brilliantly triboluminescent lanthanide complexes are found to be centrosymmetric, contrary to the expectation that triboluminescent activity derives from bulk polar charge distributions (i.e., by piezoelectrification). Crystal data for piperidinium tetrakis(benzoylacetonato)europate (**2**): monoclinic, $P2_1/n$, $a = 11.910$ (4) Å, $b = 19.667$ (8) Å, $c = 18.520$ (9) Å, $\beta = 106.07$ (3)°, $V = 4169$ Å^3, $Z = 4$, $R(F) = 3.85\%$. Crystal data for hexakis(antipyrine)terbium triiodide (**3**): rhombohedral, $R\bar{3}$, $a = 13.897$ (3) Å, $c = 31.980$ (8) Å, $V = 5349$ (2) Å^3, $Z = 3$, $R(F) = 4.47\%$. Crystal data for hexaaquadichloroterbium chloride (**4**): monoclinic, $P2/n$, $a = 7.8926$ (12) Å, $b = 6.5091$ (12) Å, $c = 9.6167$ (12) Å, $\beta = 93.751$ (12)°, $V = 493.0$ (1) Å^3, $Z = 2$, $R(F) = 2.81\%$. The structures of **2** and **4** reveal eight-coordinate, tetragonal-antiprismatic metal ion geometries, and the structure of **3** shows an octahedral environment. No single factor can account for the unexpected triboluminescence of these complexes other than the presence of easily deformable, weakly bonded interactions between ions or between ions and molecules in the lattices. On application of pressure, these weak interactions may deform to create polar domains. None of the structures displays significant disorder.

Introduction

Attempts to correlate solid-state structures with triboluminescent activity in crystalline materials are not entirely successful due primarily to their failure to account for the presence of activity in centric materials.[1] It is generally asserted that crystal cleavage resulting in light emission represents the visible evidence for the discharge of nascent charged surfaces.[2] The ability of a crystalline material to readily form charged surfaces on cleavage is a property intuitively associated with acentric, polar structures by analogy to the properties of piezoelectric materials.[3] Although numerous examples of triboluminescent activity in centric structures have been discovered in the last decade,[4] it is generally found that in groups of chemically related triboluminescent materials containing both acentric and centric members, the centric members are much less active. In fact, Zink estimates that the correlation of triboluminescence activity with noncentrosymmetric space groups is greater than 95%.[5]

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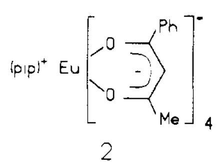
0020-1669/89/1328-1715$01.50/0

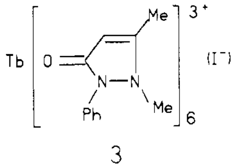
Triboluminescent complexes of the lanthanide elements are particularly interesting because the initial atmospheric dinitrogen emission may additionally excite a fluorescence emission characteristic of the metallic element. We recently reported[6] the structural characterization of the brilliantly triboluminescent compound triethylammonium tetrakis(dibenzoylmethanato)europate, $(NEt_3H)\{Eu[CH(COC_6H_5)_2]_4\}$ (**1**), in the centrosymmetric monoclinic space group *C*2/*c* but could not unambiguously distinguish it from its acentric alternative, *Cc*, by diffraction data alone.[7] The centric alternative results in a disordered structure containing two cation sites and pairs of phenyl-ring twist angles for three of the structure's four independent phenyl rings.

Subsequently, Strouse,[8] using data from an independently grown crystal of **1**, found that our coordinates could be used to construct an acentric model that produced a slightly, but significantly, lower *R* factor (when compared to our centric model) *without* further refinement. However, attempted refinement led to an unacceptable range of Eu–O distances and sets of physically unreasonable thermal parameters (as we also found), results that may be due to the computational instability of a nearly centric structure.

Since the europate salt **1** is of unrivaled triboluminescent activity, but of questioned symmetry, we have sought further examples of lanthanide complexes of comparable activity for crystallographic characterization. We now report the structures of three such complexes, all of which we find to be centric: piperidinium tetrakis(benzoylacetonato)europate (**2**), hexakis(antipyrine)terbium triiodide (**3**), and hexaaquadichloroterbium chloride (**4**). The structure of **2** has been previously reported; but refinement could be carried out only to *R* = 20%.[9] A preliminary report of the structure of **3** has appeared without atom coordinates, bond metrics, or refinement parameters.[10] The yttrium analogue of **3** has been fully characterized at *R* = 7.3%.[11] The isomorphous structures of the Nd,[12a] Sm,[12b] Gd,[12c] and Lu[12d] analogues of **4** have been determined with modern methods, but with *R* factors in the 5–8% range, compared to our 2.8%.



2



$(I^-)_3$

3

$Tb[(H_2O)_6Cl_2]Cl$

4

Experimental Section

Materials. The following reagents (supplier) were used as obtained: triethylamine (Alfa), dibenzoylmethane (Alfa), benzoylacetone (Aldrich), antipyrine (Aldrich), piperidine (Aldrich), anhydrous $Eu^{III}Cl_3$ (Aldrich), and $[Tb(H_2O)_6Cl_2]Cl$ (Alfa). **2**[13] and **3**[14] were prepared by literature methods. Anal. Calcd for **2** ($C_{45}H_{40}EuNO_8$): C, 61.22; H, 5.48; N, 1.59. Found: C, 61.15; H, 5.55; N, 1.61. Calcd for **3** ($C_{66}H_{72}I_3N_{16}O_6Tb$): C, 47.50; H, 4.35; N, 10.07. Found: C, 47.38; H, 4.34; N, 9.99. Calcd for **4** ($Cl_3H_{12}O_6Tb$): Cl, 28.49; H, 3.24. Found: Cl, 28.25; H, 3.28. Mp: **2**, 127–132 °C; **3**, 290–291 °C.

Crystallographic Structural Determinations. General Considerations. A summary of crystallographic data is collected in Table I. A Nicolet R3m/μ diffractometer with a graphite monochromator and Mo Kα radiation (λ = 0.71073 Å) was used for data collection. All samples were mounted in thin-walled capillary tubes. Empirical absorption corrections were applied in all cases. No significant decay in reflection intensities was observed for these compounds. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were treated as described separately below. SHELXTL (5.1) software was used for all calculations (G. Sheldrick, Nicolet XRD Corp., Madison, WI).

Table I. Crystallographic Data

	2	**3**	**4**
formula	$C_{45}H_{48}EuNO_8$	$C_{66}H_{72}I_3N_{12}O_6Tb$	$Cl_3H_{12}O_6Tb$
cryst syst	monoclinic	rhombohedral	monoclinic
space group	*P*2$_1$/*n*	*R*$\bar{3}$	*P*2/*n*
a, Å[a]	11.910 (4)	13.897 (3)	7.8926 (12)
b, Å	19.667 (8)		6.5091 (12)
c, Å	18.520 (9)	31.980 (8)	9.6167 (12)
β, deg	106.07 (3)		93.751 (12)
V, Å^3	4169 (3)	5349 (2)	493.0 (1)
Z	4	3	2
D(calc), g cm^{-3}	1.397	1.554	2.884
temp, °C	23	22	22
color	pale yellow	pale yellow	colorless
cryst size, mm	0.30 × 0.34 × 0.38	0.41 × 0.42 × 0.43	0.22 × 0.22 × 0.23
μ(Mo Kα), cm^{-1}	15.63	23.52	81.37
T(max)/*T*(min)	1.17	1.30	1.43
no. of rflns collected	8847	2376	2016
no. of indep rflns	8184	2105	1788
R(int), %	1.05	4.60	4.41
no. of obs rflns ($n\sigma F_o$)	5393 (n = 5)	1775 (n = 5)	1775 (n = 2.5)
2θ limits, deg	$4 \le 2\theta \le 52$	$4 \le 2\theta \le 50$	$4 \le 2\theta \le 65$
octants collected	$\pm h,+k,+l$	$+h,+k,\pm l$	$\pm h,+k,+l$
scan method	Wyckoff	$\theta/2\theta$	$\theta/2\theta$
decay, %	<1	<1	<1
R(*F*), %	3.85	4.47	2.81
$R_w(F)$, %	4.76	5.10	3.15
GOF	0.982	1.031	0.972
Δ/σ (final)	0.107	0.022	0.019
$\Delta(\rho)$, e Å^{-3}	0.70	1.28	2.01
N_o/N_v	9.97	14.38	27.5

[a] Unit cell parameters were obtained from the least-squares best fit of 25 reflections (22° ≤ 2θ ≤ 30°).

Structure of Piperidinium Tetrakis(benzoylacetonato)europate (2). The cell used in an earlier characterization of **2**[9] was reported in the monoclinic space group *P*2$_1$/*c*. The matrix (−1,0,0; 010; 101) was used to transform the cell to *P*2$_1$/*n* to take advantage of a less obtuse β angle. No violations of the systematic absences for this space group were observed at greater than 2σ. The refinement was begun by using the transformed coordinates from the previous determination.[9] Hydrogen atom contributions were idealized for the anion; all cation hydrogen atoms were found and isotropically refined.

Structure of Hexakis(antipyrine)terbium Triiodide (3). An earlier report[10] of this structure gave the space group as *R*$\bar{3}$, as did also a report of the structure of the isomorphous yttrium analogue.[11] This assignment was supported by our photographic work, which revealed $\bar{3}$ Laue symmetry, and by the centrosymmetric distribution of *E* values. Refinement of the structure in *R*$\bar{3}$ proceeded smoothly and produced a chemically acceptable set of bond parameters for the antipyrine ring. The ligand's phenyl ring was constrained to a rigid, planar hexagon (*d*(C–C) = 1.395 Å). All hydrogen atom contributions were idealized. A single peak (1.28 e Å^{-3}) dominated the final difference map at 0.98 Å from the Tb atom; this was followed by a diffuse background beginning at 0.71 e Å^{-3}.

Structure of $[Tb(H_2O)_6Cl_2]Cl$ (4). Previously reported[12a] coordinates for the isomorphous Gd analogue of **4** were used to initialize refinement. A thorough inspection of refinement in the alternative space group *Pn* revealed no evidence to support an acentric assignment. Strong correlation phenomena in the refinement process could not be dampened and inevitably led to divergence. The hydrogen atoms of the O(1) and O(2) water molecules were found and isotropically refined. The hydrogen atoms of O(3) were not found, possibly due to ambiguity in their locations relative to rotation about the Tb–O(3) axis.

Results and Discussion

In our discussion of the relationship of structure and triboluminescence activity in **1**, we suggested that the phenyl-ring and cation disorder provided a sufficient source of localized polarity to produce the observed activity.[6] We are now faced with three additional examples of very active centrosymmetric rare-earth

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(7) The centric space group was preferred for two reasons: refinement produced a narrow range of Eu–O distances, whereas acentric refinement produced a chemically unreasonable range of distances, and second-harmonic-generation studies showed only a very feeble response accountable for by trace levels of impurities.

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

	x	y	z	U^a
Eu	2974 (1)	1357 (1)	2820 (1)	37 (1)
O(1)	4366 (3)	2234 (2)	3360 (2)	43 (1)
O(2)	4836 (3)	1109 (2)	2566 (2)	54 (2)
O(3)	3544 (4)	248 (2)	3257 (2)	57 (2)
O(4)	3093 (3)	1328 (2)	4155 (2)	43 (1)
O(5)	1141 (3)	903 (2)	2870 (2)	52 (1)
O(6)	1760 (3)	2282 (2)	2992 (2)	51 (1)
O(7)	2963 (3)	2094 (2)	1796 (2)	44 (1)
O(8)	2283 (3)	744 (2)	1676 (2)	52 (2)
C(1)	5177 (5)	2499 (3)	3119 (3)	41 (2)
C(2)	5838 (5)	2155 (3)	2742 (3)	46 (2)
C(3)	5651 (5)	1473 (3)	2493 (3)	51 (2)
C(4)	3493 (5)	−99 (3)	3811 (3)	52 (2)
C(5)	3247 (6)	157 (3)	4452 (3)	60 (3)
C(6)	3052 (4)	835 (3)	4590 (3)	42 (2)
C(7)	365 (5)	1105 (3)	3160 (3)	45 (2)
C(8)	178 (5)	1778 (3)	3327 (3)	46 (2)
C(9)	870 (4)	2322 (3)	3240 (3)	41 (2)
C(10)	2942 (4)	2021 (3)	1115 (3)	38 (2)
C(11)	2675 (5)	1418 (3)	718 (3)	46 (2)
C(12)	2322 (5)	823 (3)	1009 (3)	44 (2)
C(21)	4360 (6)	3658 (3)	3137 (3)	57 (2)
C(22)	4438 (7)	4350 (3)	3181 (3)	73 (3)
C(23)	5532 (7)	4661 (3)	3349 (3)	77 (3)
C(24)	6517 (6)	4269 (3)	3464 (3)	69 (3)
C(25)	6437 (6)	3566 (3)	3398 (3)	52 (2)
C(26)	5345 (5)	3252 (3)	3241 (3)	43 (2)
C(27)	6454 (7)	1173 (4)	2068 (5)	89 (4)
C(31)	2006 (5)	1556 (3)	5296 (3)	58 (2)
C(32)	1705 (7)	1748 (4)	5938 (4)	85 (3)
C(33)	2164 (8)	1386 (4)	6587 (4)	115 (5)
C(34)	2897 (8)	849 (4)	6612 (4)	102 (4)
C(35)	3204 (6)	648 (4)	5971 (3)	74 (3)
C(36)	2753 (5)	1013 (3)	5301 (3)	49 (2)
C(37)	3700 (7)	−851 (3)	3774 (4)	85 (3)
C(41)	54 (5)	3144 (3)	4027 (4)	67 (3)
C(42)	−150 (6)	3807 (4)	4223 (5)	89 (4)
C(43)	138 (6)	4347 (4)	3835 (5)	94 (4)
C(44)	620 (6)	4233 (3)	3247 (4)	82 (3)
C(45)	842 (5)	3576 (3)	3061 (4)	61 (2)
C(46)	561 (5)	3023 (3)	3444 (3)	48 (2)
C(47)	−391 (6)	557 (3)	3359 (4)	68 (3)
C(51)	3796 (5)	3176 (3)	1155 (3)	57 (2)
C(52)	4019 (7)	3781 (3)	833 (4)	72 (3)
C(53)	3610 (6)	3868 (3)	71 (4)	66 (3)
C(54)	2987 (6)	3360 (3)	−361 (3)	62 (3)
C(55)	2790 (5)	2757 (3)	−45 (3)	53 (2)
C(56)	3195 (4)	2653 (2)	723 (3)	38 (2)
C(57)	1923 (6)	229 (3)	492 (3)	65 (3)
Pn	8888 (4)	2347 (2)	9652 (2)	46 (2)
Pc(1)	9980 (5)	2514 (3)	10232 (4)	58 (2)
Pc(2)	9840 (5)	2453 (3)	11016 (3)	64 (3)
Pc(3)	9371 (7)	1758 (4)	11133 (4)	72 (3)
Pc(4)	8281 (7)	1591 (4)	10528 (4)	64 (3)
Pc(5)	8445 (5)	1662 (3)	9754 (3)	51 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

complexes, none of which show crystallographically discernible disorder except for possible disorder in the hydrogen-bonded networking in **4**.

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

	x	y	z	U^a
Tb	0	0	0	33 (1)
I(1)	0	0	5000	109 (1)
I(2)	0	0	2095 (1)	83 (1)
O	−304 (4)	1112 (3)	412 (1)	51 (2)
C(3)	−272 (5)	1831 (5)	667 (2)	46 (2)
N(2)	−417 (5)	2691 (4)	525 (2)	53 (2)
N(1)	−447 (6)	3275 (5)	865 (2)	71 (3)
C(4)	−253 (7)	2850 (7)	1207 (2)	76 (4)
C(5)	−153 (6)	1936 (6)	1097 (2)	62 (3)
C(21)	−228 (8)	4437 (7)	810 (3)	96 (5)
C(31)	−157 (11)	3321 (10)	1630 (3)	128 (9)
C(11)	−361 (4)	2716 (4)	−224 (1)	64 (3)
C(12)	−865	2637	−610	98 (6)
C(13)	−1917	2533	−626	126 (7)
C(14)	−2464	2507	−257	127 (7)
C(15)	−1960	2585	128	89 (4)
C(16)	−909	2690	145	51 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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

	x	y	z	U^a
Tb	2500	1529.8 (2)	2500	15.9 (1)
Cl(1)	2604 (2)	−1623 (1)	594 (1)	27 (1)
Cl(2)	2500	3749 (2)	7500	30 (1)
O(1)	−414 (3)	510 (4)	2182 (3)	29 (1)
O(2)	879 (3)	4254 (4)	1462 (3)	29 (1)
O(3)	1070 (4)	2995 (5)	4383 (3)	29 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Bond Distances and Angles for Piperidinium Tetrakis(benzoylacetonato)europate (**2**)

	(a) Bond Distances (Å)		
Eu–O(1)	2.409 (3)	Eu–O(6)	2.398 (4)
Eu–O(2)	2.440 (4)	Eu–O(7)	2.384 (3)
Eu–O(3)	2.361 (4)	Eu–O(8)	2.378 (3)
Eu–O(4)	2.438 (3)	Eu–O (av)	2.399 (5)
Eu–O(5)	2.384 (4)		
	(b) Bond Angles (deg)		
O(1)–Eu–O(2)	70.5 (1)	O(5)–Eu–O(6)	71.7 (1)
O(3)–Eu–O(4)	72.6 (1)	O(7)–Eu–O(8)	71.1 (1)

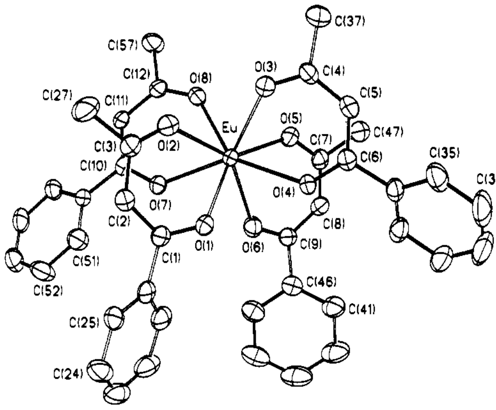

Figure 1. Structure of the anion of **2**.

The structure of piperidinium tetrakis(benzoylacetonato)europate (**2**) is particularly unrevealing. From the complete absence of violations greater than 2σ to the systematic absences for the space group, $P2_1/n$, the assignment of centrosymmetry to **2** is made without ambiguity. No evidence for disorder in either the cation or anion was resolvable from our data, nor do any of the thermal parameters suggest the possibility of disorder masked by thermal activity. Many aspects of the structure have been previously discussed[9] and need not be repeated in detail. The eight-coordinate geometry is tetragonal antiprismatic, the tetragonal planes being [O(1),O(2),O(3),O(4)] and [O(5),O(6),O(7),O(8)] (see Figure 1). The complex possesses an approximate 2-fold rotational axis (vertical in Figure 1). About a plane perpendicular to this axis, the methyl groups lie to one side and the phenyl groups to the other. This maximization of polarity may be due to the polar nature of the medium (excess amine) used in the reaction to form **2**. The average Eu–O distances in **1** (2.39 (1) Å)[6] and **2** (2.399 (5) Å) are the same, although in **2** a slightly greater range (2.36–2.41 Å for **1** and 2.36–2.44 Å for **2**) of Eu–O distances reflects the lower symmetry of **2**. As was also true for **1**, the ions of **2** are strongly H-bonded. the piperidine N-bound protons

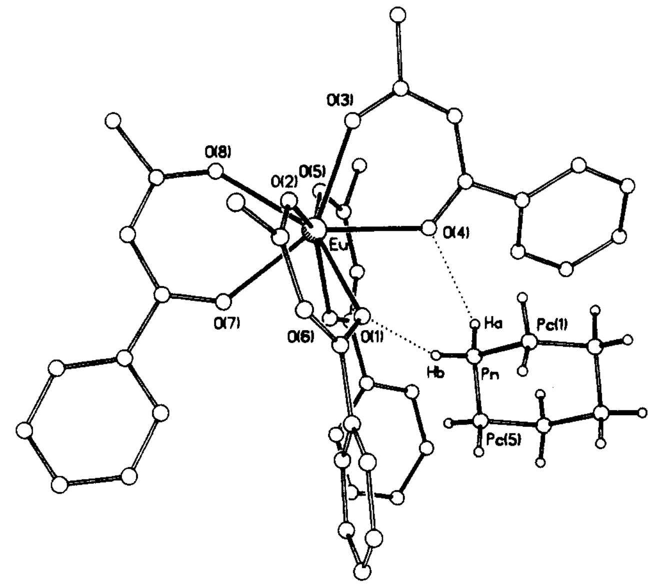

Figure 2. View of **2** showing the strong hydrogen-bonded interionic association: O(1)-Hb = 1.94 (3) Å; O(2)-Ha = 2.19 (3) Å.

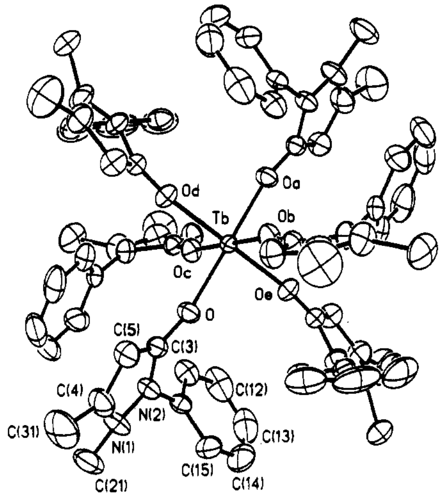

Figure 3. Structure of the cation of **3**.

(crystallographically located) make contacts of 1.94 (3) Å with O(1) [N···O(1) = 2.734 (7) Å] and 2.19 (3) Å to O(4) [N···O(4) = 2.836 (7) Å]. Both of the oxygen atoms forming these interactions are adjacent to phenyl-substituted carbon atoms, requiring cation approach toward the presumably more crowded phenyl side of the anion. The question of the role hydrogen bonding plays in triboluminescent activity is a curious one, but it may provide a location for a pressure-induced deformation of a centric lattice along natural cleavage planes. In a series of triboluminescent anthracyl alcohols recently studied, the role of hydrogen bonding was discussed.[4]

Hexakis(antipyrine)terbium triiodide (**3**) crystallizes in the rhombohedral space group $R\bar{3}$; our results closely agree with those found for its isomorphous yttrium analogue.[11] The Tb atom coordination environment is only slightly distorted from octahedral symmetry. The Tb atom residues at a site of $\bar{3}$ symmetry. Nothing in our data or in those reported for the yttrium analogue[11] provides any suggestion of a possible reassignment to the acentric alternative space group $R3$. In addition, a comparison of Bijvoet pairs for **3** revealed no systematic discrepancies, and nothing indicates that crystallographically recognizable disorder or unusual thermal activity is present in this complex. The iodide counterions are essentially noninteracting; the two shortest interionic contacts, H(5)···I(2) = 3.31 (2) Å and H(13)···I(1) = 3.40 (2) Å, are both too long to suggest that they are significantly involved in charge redistribution.

Table VI. Bond Distances and Angles for Hexakis(antipyrene)terbium Triiodide (**3**)

(a) Bond Distances (Å)			
Tb-O	2.226 (4)	C(4)-N(1)	1.332 (12)
O-C(3)	1.273 (8)	N(1)-N(2)	1.371 (9)
C(3)-C(5)	1.387 (9)	N(2)-C(3)	1.384 (10)
(b) Bond Angles (deg)			
O-Tb-Oa	180	N(2)-C(3)-C(5)	107.3 (6)
O-Tb-Ob	88.5 (1)	C(3)-C(5)-C(4)	106.5 (7)
O-Tb-Oc	91.5 (1)	C(5)-C(4)-N(1)	109.5 (7)
Tb-O-C(3)	168.5 (4)	C(4)-N(1)-N(2)	108.5 (8)
O-C(3)-C(5)	132.3 (7)	N(1)-N(2)-C(3)	108.1 (5)
O-C(3)-N(2)	120.4 (5)		

Table VII. Bond Distances and Angles for $[Tb(H_2O)_6Cl_2]Cl$ (**4**)

(a) Bond Distances (Å)			
Tb-Cl(1)	2.756 (1)	O(1)-H(1a)	1.01 (3)
Tb-O(1)	2.394 (2)	O(1)-H(1b)	0.99 (2)
Tb-O(2)	2.368 (2)	O(2)-H(2a)	1.00 (5)
Tb-O(3)	2.394 (3)	O(2)-H(2b)	1.00 (2)
O(1)···Cl(1c)	3.168 (4)	O(3)···Cl(1a)	3.183 (4)
O(1)···Cl(2b)	3.249 (4)	O(3)···Cl(1d)	3.171 (4)
O(2)···Cl(1b)	3.147 (5)	O(3)···Cl(2)	3.171 (5)
(b) Bond Angles (deg)			
Cl(1)Tb-Cl(1a)	83.81 (7)	O(1)-Tb-O(3)	73.2 (1)
Cl(1)-Tb-O(1)	77.2 (1)	O(1)-Tb-O(1a)	147.8 (1)
Cl(1)-Tb-O(2)	108.4 (1)	O(1)-Tb-O(2a)	138.5 (1)
Cl(1)-Tb-O(3)	146.7 (1)	O(1)-Tb-O(3a)	120.7 (1)
Cl(1)-Tb-O(1a)	79.0 (1)	O(2)-Tb-O(3)	75.7 (1)
Cl(1)-Tb-O(2a)	143.0 (1)	O(2)-Tb-O(2a)	83.0 (1)
Cl(1)-Tb-O(3a)	76.0 (1)	O(2)-Tb-O(3a)	69.6 (1)
O(1)-Tb-O(2)	70.5 (1)	O(3)-Tb-O(3a)	133.1 (1)

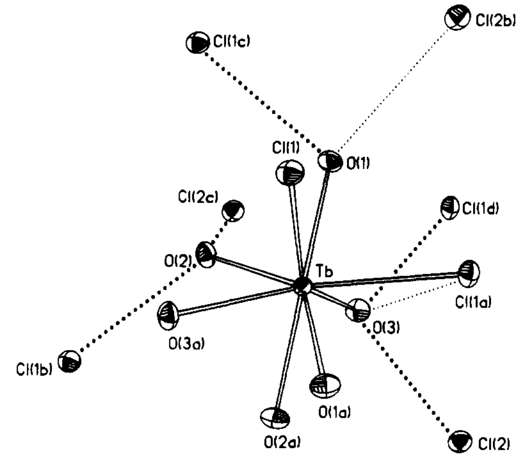

Figure 4. Coordination sphere for **4** with nearest-neighbor hydrogen-bonded interactions (distances given in Table VII).

Unlike complexes **2**[13] and **3**,[14,15] whose triboluminescent activity has been previously reported, that of hexaaquadichloroterbium chloride (**4**) has, to our knowledge, not been noted. The lanthanide dichloro hexahydrate chlorides form an isomorphous series from Nd to Lu; several of the chloride salts of the hexahydrates have been fully characterized,[12] but never the terbium salt, and none previously with found hydrogen atoms, information vital to a discussion of hydrogen bonding.

In agreement with the previous determinations of this series of structures,[12] we find evidence that supports only the selection of $P2/n$ as the correct space group. Again, an examination of Bijvoet pairs shows no systematic discrepancies. The structure is a distorted square antiprism with the distortions due to the difference in Tb-O and Tb-Cl distances. The square planes are [Cl(1),Cl(1a),O(1a),O(3a)] and [O(1),O(3),O(2a),O(2)]. Figure 4 shows the shortest O-H···Cl⁻ hydrogen bonds given as O···Cl⁻ distances. The hydrogen atoms of O(1) and O(2) were easily

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(15) Hurt, C. R.; McAvoy, N.; Bjorklund, S.; Filipescu, N. *Nature* **1966**, *212*, 179.

found from difference maps, but those of O(3) could not be found. A range of acceptable hydrogen-bond distances for O–H···Cl interactions, given as O···Cl$^-$ distances, is 2.86–3.21 Å.[16] Within this range O(1) forms one long hydrogen bond, O(2) forms two, but O(3) forms three. Since the three chloride ions bound to O(3) form angular relationships incompatible with simultaneous three-way hydrogen bonding, we conclude that the O(3) water molecule is rotationally disordered, thus accounting for our inability to locate crystallographically its hydrogen atoms.

The three lanthanide complexes whose structures we report display, as the most visible component of their tribolumunescent emission, the characteristic photoluminescence of the metallic element.[17] Thus, the terbium complexes emit green light and the europium complex emits red light. A complete discussion of the solid and solution emission and excitation spectra of these and related complexes, and the small perturbations in energies deriving from triboexcitation, will be the subject of a future paper.

The involvement of gaseous dinitrogen (or other gases with suitable physical properties) in triboluminescent emission has been studied by Zink;[4d] its essential presence in the activity of the three compounds we studied is demonstrated by the following observations. When crystals are grown and cleaved under a helium atmosphere, no emission is observed, when crystals are grown under a dinitrogen atmosphere but cleaved under helium, almost full activity is seen, and when crystals are grown in helium but cleaved under dinitrogen, weak activity is seen. This set of observations further demonstrates that dinitrogen trapped in the crystal lattice is more important than external dinitrogen in determining the intensity of emission and suggests that one element in determining the relative emission intensities of a series of related materials may be the differences in the abilities of these crystalline lattices to trap and retain gases of appropriate ionization energies.

Conclusions

We have determined with modern precision the crystal structures of three brilliantly triboluminescent lanthanide complexes, one unambiguously centrosymmetric and the other two centrosymmetric, to the limits of certainty crystallographic methods can provide. Earlier we concluded[6] that **1** (whose centrosymmetry has been questioned[8]) derived its triboluminescent activity from polar domains created by disorder in the cation sites and the resulting disorder in the phenyl rings. A similar effect is not evident in **2**, which is, of the three structures we now report, the closest analogue to **1**; both are aliphatic amine salts of eight-coordinate tetrakis(β-diketone) complexes. Both **1** and **2** show unusually close N–H···O interionic contacts, 2.82 Å for **1**[6] and 2.73 and 2.84 Å for **2** (given as N···O distances). The role, if any, these notably close contacts play in determining triboluminescent activity is questionable in light of a second structure we reported[6] of **1** whose lattice contained cocrystallized CH_2Cl_2; this structure is also centrosymmetric but is not disordered, has an only slightly longer N–H···O contact (2.86 Å), and is without triboluminescent activity. When the solvated version of **1** is allowed to desolvate under reduced pressure, full activity is restored.[6]

The hexakis(antipyrine) complex **3** offers no obvious structural basis for triboluminescent activity. One may note the ease of polarization of iodide ions as a source of charge deformation, but no series of isomorphous halide salts has been shown to increase in activity down the periodic table, and, of course, the vast majority of iodide salts are inactive. Furthermore, the positive charge in **3** is likely significantly delocalized to the ligands, reducing the ability of the cation to produce strong polarizations.

Finally, the terbium hexahydrate **4**, which exists in a complex hydrogen-bonded network, may derive its activity from pressure-sensitive deformations of the network in which alternative O–H···Cl$^-$ interactions become more important with an increase in pressure.

The contribution of defect structures and impurities to the emission processes has been studied.[4a] Each, or all, of the structures we studied may contain local acentric domains. The specimens selected for crystallographic data collection are the most defect-free specimens available (by optical microscopy) and may not be fully representative of the bulk sample. However, we observe no difference in activity among fractions of the bulk samples separated according to visible defects, nor have we seen differences in activity for the same polymorph among samples formed by different crystal growth techniques.

From evidence derivable from our crystallographic data, all of these centrosymmetric, actively triboluminescent complexes likely obtain the polar characteristics (local piezoelectricity) essential to their activity from several sources having in common weak interionic interactions capable of deformation on application of pressure. At some critical pressure, the crystal cleaves, but at the leading edge where pressure is greatest, charged surfaces form. While the bulk of the crystal relaxes to its original centrosymmetric form,[18] the charged surfaces discharge and excite, via the intermediacy of dinitrogen, photoluminescent emission from the lanthanide complexes. The three structures we report are all ionic solids that can cleave along intrinsically charged planes (although such cleavage will be resisted by Coulombic forces), allowing nonpiezoelectric surface-charging pathways.[4a,b] Zink has suggested that only a relatively small fraction of cleavages along such planes may be sufficient to explain the observation of activity in centric materials.[4b]

Acknowledgment. We thank Linda M. Sweeting for stimulating our interest in the structural study of triboluminescent materials, for helpful discussions, and for assistance in determining the fluorescence spectra.

Supplementary Material Available: Tables 2–5, listing bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (9 pages); Table 1, listing observed and calculated structure factors (54 pages). Ordering information is given on any current masthead page.

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[17] Sinha, A. P. B. *Spectrosc. Inorg. Chem.* **1971**, *2*, 255.

[18] Zink et al. have shown in a series of platinum complexes that triboluminescence occurs near atmospheric pressure: Leyrer, E.; Zimmermann, F.; Zink, J. I.; Gliemann, G. *Inorg. Chem.* **1985**, *24*, 102.