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A triboluminescent europium(III) complex

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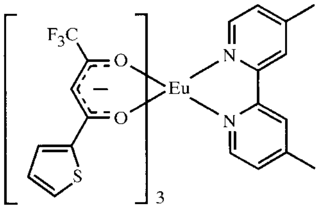
The crystal structure of (4,4′-dimethyl-2,2′-bipyridyl)tris[3,3,3-trifluoro-1-(2-thenoyl)propan-2-onato]europium(III), or more commonly (4,4′-dimethyl-2,2′-bipyridyl)tris(2-thenoyltrifluoroacetonato)europium(III), [Eu($C_8H_4F_3O_2S$)$_3$($C_{12}H_{12}N_2$)], has been determined. Crystals of the complex emit vivid red light when scratched or fractured. This triboluminescent activity seems to correlate with the non-centrosymmetric crystal structure and disorder of the thienyl rings and CF_3 groups which is present here and in similar compounds. While modeling the thienyl-ring disorder, it was noted that the bond angle at the C atom replaced by S is a sensitive sign of even small rotational ring disorder. The coordination geometry of the Eu^{III} ion can be described as square antiprismatic, with coordination by the six O atoms of the three chelating *β*-diketonate ligands and the two N atoms of the neutral bipyridyl ligand.

Comment

Triboluminescence, the process whereby certain materials emit light when they are fractured, has been known for nearly 400 years (Walton, 1977). Although it remains an obscure phenomenon, the effect is generally explained in terms of excitation of the molecule by an electric discharge between the surfaces of the fractured crystals and subsequent fluorescence (Sweeting *et al.*, 1997). Recently, a novel and potentially important application of the phenomenon has been proposed for the development of real-time damage sensors in composite materials (Sage *et al.*, 1999). Specifically, the idea is built on the observation that light emission occurs when a composite material containing the triboluminescent molecule is damaged. Monitoring the wavelength and measuring the amount of emission would then yield information on the location and extent of the damage, respectively. Preliminary experiments have demonstrated the validity of such a concept.

In the course of our studies of lanthanide phosphors for organic electroluminescence applications (Wang *et al.*, 2001), we synthesized a europium(III) complex, namely (4,4′-dimethyl-2,2′-bipyridyl)tris(2-thenoyltrifluoroacetonato)europium(III), [Eu(DMDPY)(TTA)$_3$], (I), and inadvertently observed its triboluminescence. Brilliant red sparks were displayed when crystals of the complex were cut or crushed, even with room illumination on. We report herein the solid-state structure of this complex, which has been important in understanding the observed triboluminescence. A literature search for related compounds indicated that the synthesis (Shang *et al.*, 1997; Chen *et al.*, 1998), triboluminescent property (Chen *et al.*, 1999) and crystal structure (Chen *et al.*, 1999) of a closely related compound, the 2,2′-bipyridyl adduct of tris(2-thenoyltrifluoroacetonato)europium(III), (II), have recently been reported.



(I)

Compound (I) crystallizes in the polar space group *Pca*2$_1$, with four molecules in the unit cell. The asymmetric unit contains only one molecule (Fig. 1). The Eu^{III} ion is eight-coordinated by six O atoms of the three chelating *β*-diketonate ligands and by two N atoms of a 4,4′-dimethyl-2,2′-bipyridyl ligand. The coordination polyhedron can be best described as being square antiprismatic. The two square planes with respective deviations of 0.0486 (14) and 0.0972 (13) Å are O11/O21/N14/N124 and O12/O22/O13/O23. Corresponding values (0.0458 and 0.0124 Å, respectively) of this structural parameter are somewhat smaller in the structure of (II) (Chen *et al.*, 1999). It appears that the methyl substituents on the 4,4′-dimethyl-2,2′-bipyridyl ligand cause the square antiprism to distort slightly. The distance from the metal ion to the O11/O21/N14/N124 plane is 1.4198 (14) Å, which is significantly longer than that to the other plane, O12/O22/O13/O23, of 1.2116 (13) Å. The dihedral angle between the two planes is 3.65 (7)°, which is somewhat larger than that (2.6°) found in the structure of (II). All observed bond lengths and angles are normal. The average Eu—O and Eu—N bond lengths are 2.37 (2) and 2.582 (8) Å, respectively. These values are unremarkably similar to those found for (II) (2.352 and 2.578 Å, respectively). The mean O—Eu—O angle within the chelate rings is 71.9 (7)°, which is close to that found in (II) (72.1°).

The observed triboluminescent activity of (I) is in line with the commonly accepted mechanism for triboluminescence, the first step being charge separation due to piezoelectricity which occurs when the non-centrosymmetric crystal is deformed or fractured (Longchambon, 1923). In this context, it is worth noting that complex (II), which differs from (I) only in the absence of two methyl substituents on the bipyridyl ligand, is

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also triboluminescent, but crystallizes in a monoclinic centrosymmetric space group $P2_1/n$ (Chen *et al.*, 1999). The authors ascribe the observed triboluminescence to the disorder of the thienyl rings and CF_3 groups of the β-diketonate ligands. Impurities have also been suggested to play important roles in the triboluminescent activity of some centrosymmetric materials (Rheingold & Sweeting, 1987; Sweeting *et al.*, 1997). Both the structural disorder and impurities in crystals are believed to create the localized asymmetry that is essential to support charge separation, and could therefore explain why materials that are symmetric overall can still exhibit triboluminescence.

These facts led us to examine the disorder present in (I) very carefully. The CF_3 groups are slightly disordered in (I) due to rotation about the C—C bond. Such distortions are commonly observed in β-diketonates substituted with CF_3 groups even at reduced temparatures and are well modeled using anisotropic displacement parameters. In addition, two of the three thienyl rings show apparent disorder. For ring 3, this was evidenced, before disorder modeling, by an abnormally large S-atom displacement parameter ($U_{\rm iso}$ = 0.075 Å^2) and an abnormally small ($U_{\rm iso}$ = 0.032 Å^2) *ortho*-C-atom displacement parameter. In ring 2, the difference in displacement parameters was much smaller ($U_{\rm iso}$ = 0.056 and 0.050 Å^2) and disorder was not obvious until the bond distances and angles in the ring fragments were examined and a marked difference in the geometry of rings 2 and 1 was noticed. In particular, the C3—C4—C5 angle in ring (I) measured 113.7 (5)°, while that in ring 2 measured 111.5 (5)°. In clearly disordered ring 3, the C3—C4—C5 angle was 98.4 (4)°. The displacement parameters of all five atoms in ring 1 were in the range $U_{\rm iso}$ = 0.042–0.057 Å^2, with a difference of $U_{\rm iso}$ = 0.005 Å^2 between the S and *ortho*-C atom values. Abnormal displacement parameters alone are not sufficient to reveal all cases of disorder.

We conducted a search of the Cambridge Structure Database (CSD; Allen & Kennard, 1993) for thiophene rings substituted at the 5-position (our numbering). We found 378 entries containing 613 of these pendant thienyl groups, of which 130 entries (232 fragments) have a disorder flag which ususally, but not necessarily, involves the thienyl ring. In either case, we found the distributions of bond lengths and angles to be very broad and in general bimodal. This was most evident for the entries without disorder flags when looking at the bond angle at C4, the *ortho*-C atom, which would be substituted by S in the case of ring rotation. The distribution ranged from 91.0 to 123.0° in a roughly Gaussian shape [11° FWHM (full width at half maximum)], peaking at 109° and included a sharp (2° FWHM) spike at 112.5° with over twice the intensity of the Gaussian peak. Closer examination of a few randomly selected entries revealed that most of those within the spike had little or no signs of thienyl disorder, while those with angles below 109° showed abnormal displacement parameters, increased *R* values and/or other abnormal bonding parameters which could indicate rotational ring disorder. Our ring 1 compared favorably with those chosen from within the spike and was declared disorder free and fit to be used as a good restraint model for the two disordered rings. If it holds true that undisordered thienyl rings have a mean *ortho*-C angle of 112.5°, then approximately half of the CSD entries with a thienyl ring within the molecule have unresolved disorder. This unresolved disorder might explain some mysterious cases of triboluminescence or provide new compounds to examine in the search for further triboluminescent compounds.

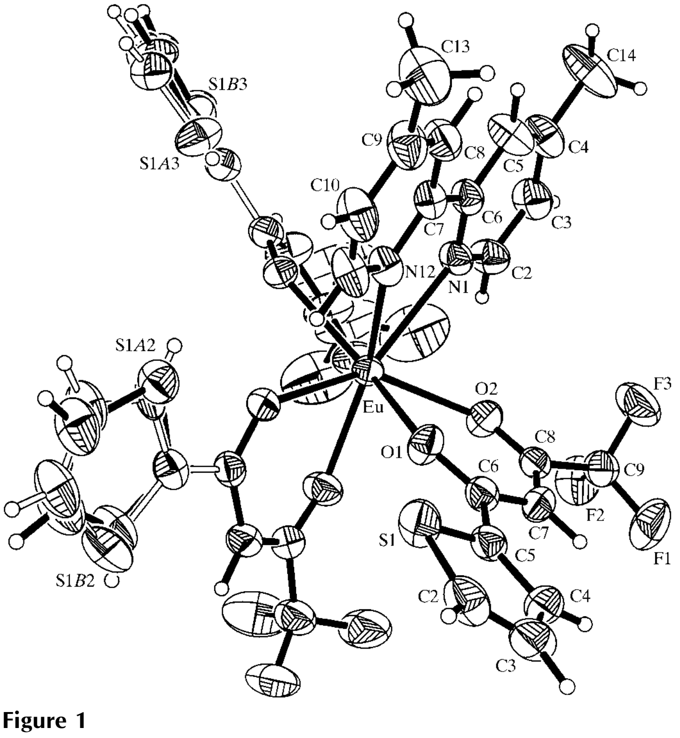

Figure 1
Displacement ellipsoid plot of the title compound with ellipsoids at the 50% probability level.

Experimental

To a solution prepared from KO^tBu (1.12 g, 10.0 mmol) in H_2O (20 ml) was added thenoyltrifluoroacetone (TTA; 2.20 g, 9.9 mmol). The clear mixture was added to an aqueous solution of $EuCl_3\cdot6H_2O$ (1.20 g, 3.3 mmol in 20 ml H_2O) to yield a white precipitate. The mixture was stirred at 333 K for 20 min and then for 3 h at room temperature. The precipitate was filtered off, washed with water (2 × 50 ml), and dried at 313 K under vacuum for 12 h. The aqua complex of tris(2-thenoyltrifluoroacetonato)europium(III) was obtained as colorless crystals after recrystallization from acetone (2.38 g, 85% yield). Following the procedure developed by Melby (Melby *et al.*, 1964), complex (I) was prepared by substituting the coordinated water molecule in the aqua complex with 4,4′-dimethyl-2,2′-bipyridyl as the neutral ligand. Characterization data for (I), ^{1}H NMR (250 MHz, CD_3Cl, δ, p.p.m.): 3.32 (*s*, 3H, TTA), 4.68 (*s*, 6H, CH_3), 6.11 (*s*, 3H, TTA), 6.50 (*s*, 3H, TTA), 7.35 (*s*, 2H, DMDPY), 8.50 (*s*, 2H, DMDPY), 9.20 (*s*, 2H, DMDPY), 14.8 (*s*, 3H, CH); FAB–MS: 1001.76 $[M + H]^+$, 779.6 $[M - \text{TTA}]^+$. Analysis calculated for $C_{36}H_{24}EuF_9N_2O_6S_3$: C 43.24, H 2.42, N 2.80%; found: C 43.04, H 2.28, N 2.81%.

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Crystal data

$[Eu(C_8H_4F_3O_2S)_3(C_{12}H_{12}N_2)]$
$M_r = 999.71$
Orthorhombic, $Pca2_1$
$a = 20.781$ (2) Å
$b = 10.7159$ (12) Å
$c = 17.8255$ (19) Å
$V = 3969.6$ (7) Å^3
$Z = 4$
$D_x = 1.673$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 5605 reflections
$\theta = 2.1$–29.6°
$\mu = 1.83$ mm^{-1}
$T = 170$ (2) K
Block, light orange
0.30 × 0.30 × 0.20 mm

Data collection

Bruker CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{\min} = 0.610$, $T_{\max} = 0.712$
47 819 measured reflections
9109 independent reflections
7963 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.035$
$\theta_{\max} = 27.6°$
$h = -26 \rightarrow 26$
$k = -13 \rightarrow 13$
$l = -23 \rightarrow 23$
344 standard reflections every 1818 reflections intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.062$
$S = 1.12$
9109 reflections
588 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0226P)^2 + 1.4129P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.020 (7)

H atoms were added at idealized positions, constrained to ride on the atom to which they are bonded (C—H = 0.95 or 0.98 Å) and given displacement parameters equal to 1.2 or 1.5 times $U_{\rm iso}$ of the bonded atom. Two of the three thienyl rings showed rotational disorder and were modeled as two overlapping fragments. The refined populations of the major fragments were 0.713 (4) and 0.968 (4) for rings 3 and 2, respectively. To prevent ring deformations and to account for large correlations in atomic positions of overlapping sites, the split rings were restrained to have approximately the same geometry as the single ordered ring, ring 1, in the structure. Overlapping atoms were restrained to have similar displacement parameters. The eight largest residual peaks in the final difference map (0.50–0.69 e Å^{-3}) were located less than 1.0 Å from the Eu atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1611). Services for accessing these data are described at the back of the journal.

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