

## The Crystal Structure of Europium Tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione] Dihydrate

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*The crystal structure of europium tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione] dihydrate has been determined from visually estimated intensity data for 1444 independent reflections. The crystals are monoclinic, space group  $P2_1/c$  with 4 molecules per unit cell. The cell dimensions are  $a = 11.40(2)$  Å,  $b = 22.40(3)$  Å,  $c = 13.72(2)$  Å,  $\beta = 105.0(1)^\circ$ . The europium atoms are each coordinated by 8 oxygen atoms arranged at the vertices of an archimedean antiprism. One  $\beta$ -diketone group has its oxygen atoms at the adjacent corners of one square while the other two groups both have one oxygen atom at a corner of each square. Two water molecules at diagonally opposite corners of one square complete the coordination. Due to a slow decomposition of the crystals the X-ray data was not complete or accurate enough to give accurate atomic positions and only the general outline of the molecular geometry can be discussed.*

### Introduction

The ease of formation and the stability of the tetrakis chelates of lanthanide ions with substituted  $\beta$ -diketones<sup>1</sup> have given rise to many structural studies (e.g.<sup>2,3</sup>) of these compounds over the past decade. The interest has been largely in the inorganic and structural chemistry, particularly the configuration of the liganding groups around the central ion. The corresponding neutral tris chelates have been much less studied. The present investigation, which was begun at RCA Laboratories, Princeton, N.J., U.S.A., was undertaken in order to elucidate the stereochemistry of the compound europium tris[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione] dihydrate which had been found to be a laser.<sup>4</sup> The main structural features are described in the present paper. Unfortunately the accuracy is quite low due to a slow decomposition of the crystals and precise details of the nature of the bonding involved have not been obtained.

\* Throughout this paper the standard deviations of distances and angles are shown in brackets.

### Experimental

#### Crystal Data

$\text{EuC}_{24}\text{H}_{16}\text{O}_8\text{S}_3\text{F}_9$ ,  $M = 851.6$ . Monoclinic,  $a = 11.40(2)$  Å,  $b = 22.4(3)$  Å,  $c = 13.72(2)$  Å,  $\beta = 105.0(1)^\circ$ ,  $V = 3383$  Å<sup>3</sup>. Absent spectra:  $h0l$  with  $l$  odd,  $0k0$  with  $k$  odd. Space group  $P2_1/c$ ,  $Z = 4$ .  $d_{\text{calc}} = 1.673$  g cm<sup>-3</sup>.  $\mu(\text{MoK}\alpha) = 21.4$  cm<sup>-1</sup>.

The crystals, as prepared, decomposed in air in 1–2 hours. Since they could be kept for months in a desiccator unchanged, the decomposition reaction appeared to be a hydrolytic one. Coating the crystals with a thin film of paraffin, or sealing them in capillaries, slowed down the decomposition considerably, but under X-radiation deterioration in crystal quality always occurred.

The procedure followed in the collection of three dimensional data was to repeat a standard photograph after each layer line had been recorded by the equi-inclination Weissenberg technique. If signs of serious deterioration appeared the crystal was replaced by another of as close to the same size and shape as possible. The average size of the crystals used for the  $c$  axis rotation was 0.15 mm on edge of a square cross section and 0.5 mm in length along the original needle or crystallographic  $c$  axis.

The bulk of the data was taken from the 12 reciprocal lattice layers  $hk0$ – $hk11$ , while the  $h0l$ ,  $h1l$ ,  $h2l$  and  $0kl$ ,  $1kl$  and  $2kl$  reflections were used to complete the data and to establish scaling factors for the separate layers of the  $c$  axis rotation. Due to the difficulty of cutting the crystals across the needle those used for the  $a$  and  $b$  axis rotations had cross sections of about 0.3 by 0.15 mm and the scaling of the  $c$  axis rotation layers was rather unsatisfactory. At a late stage in the analysis these were rescaled against the calculated  $F$ 's.  $\text{MoK}\alpha$  (Zr filtered) was used throughout and intensities were estimated visually by comparison with a standard scale. Cylindrical absorption corrections were made by approximating the measured cross sectional area of each crystal to a circle of equal area. The data was very incomplete, because of, in addition to the crystal deterioration mentioned above, inherent disorder or high thermal motion in certain

TABLE I. Coordinates of the Atoms.

Atom	x	y	z	B(Å <sup>2</sup> )	Atom	x	y	z	B(Å <sup>2</sup> )
Eu	0.1861	0.0033	0.1969	3.6	C(14)	0.047	-0.145	0.217	4.9
S(1)	0.5473	0.0814	0.0760	7.0	C(15)	0.168	-0.145	0.208	5.4
O(1)	0.0683	0.0839	0.1100	3.8	C(16)	0.249	-0.197	0.258	6.3
O(2)	0.3177	0.0595	0.1217	3.7	F(4)	0.344	-0.189	0.319	14.4
C(1)	0.636	0.129	0.040	7.4	F(5)	0.197	-0.244	0.276	10.0
C(2)	0.579	0.186	0.019	5.9	F(6)	0.290	-0.217	0.179	12.2
C(3)	0.460	0.192	0.041	4.0	S(3)	0.1087	-0.1175	0.4937	7.7
C(4)	0.430	0.133	0.074	4.6	O(5)	0.2226	0.0871	0.3078	4.8
C(5)	0.319	0.112	0.097	2.6	O(6)	0.1549	-0.0275	0.3609	3.9
C(6)	0.223	0.156	0.090	3.7	C(17)	0.097	-0.136	0.617	9.4
C(7)	0.107	0.134	0.088	5.9	C(18)	0.125	-0.079	0.665	5.9
C(8)	0.013	0.183	0.081	4.4	C(19)	0.139	-0.028	0.627	4.9
F(1)	-0.092	0.171	0.026	7.4	C(20)	0.129	-0.044	0.527	3.8
F(2)	0.034	0.236	0.051	9.8	C(21)	0.177	-0.003	0.454	4.7
F(3)	-0.011	0.196	0.167	10.6	C(22)	0.202	0.056	0.477	3.7
S(2)	-0.2693	-0.0554	0.1577	7.6	C(23)	0.219	0.093	0.399	5.2
O(3)	0.2322	-0.1005	0.2013	3.7	C(24)	0.272	0.157	0.450	10.2
O(4)	-0.0143	-0.0486	0.1610	3.4	F(7)	0.361	0.174	0.423	15.9
C(9)	-0.384	-0.092	0.191	8.4	F(8)	0.218	0.196	0.388	16.9
C(10)	-0.335	-0.145	0.219	8.4	F(9)	0.261	0.176	0.523	16.2
C(11)	-0.217	-0.162	0.235	2.8	O(7)	0.4040	-0.0095	0.3019	6.2
C(12)	-0.163	-0.110	0.191	4.9	O(8)	0.1433	-0.0258	0.0146	5.5
C(13)	-0.043	-0.098	0.183	4.3					

parts of the structure. Very few reflections with  $d < 1.1 \text{ \AA}$  were observed. Intensity estimates were obtained for 1444 independent reflections. The intensities were converted to a set of F values by the usual Lorentz-polarization corrections.

#### Structure Determination and Refinement

The Eu atom positions were found directly from the sections of the three dimensional Patterson function at  $x, 1/2, z$ ;  $x, y, 1/2$ . The  $F^2$  data were sharpened to correspond to that of atoms at rest. Since the y coordinates of the Eu atoms were almost exactly 0 and  $1/2$  there was no Eu contribution to the reflections with  $k + l$  odd. A three dimensional electron density map was computed using the phase angles calculated from the Eu positions, and this included therefore a false mirror plane  $x, 0, z$ . Although the resolution was poor, particularly in the regions of the  $-\text{CF}_3$  groups, no great difficulty was experienced in disentangling the molecule from its superposed image.

The model deduced for the molecule and two water molecules coordinated to the Eu atom was refined first by the computation of seven successive sets of  $\rho_{\text{obs}}$  and  $\rho_{\text{obs}} - \rho_{\text{calcd}}$  electron density maps. For all observed reflections R was reduced to 0.123. Least squares refinement was then carried out using the diagonal matrix approximation and R was reduced to 0.115. The above calculations were carried out on the RCA 601 computer and the Fordham University IBM 360 computer using programs written by the

author. Finally, three cycles of full matrix refinement using the Busing-Levy program<sup>5</sup> were carried out on the New York University CDC 6600 computer. Unit weights were used and the final value of R was 0.111 and that of wR 0.147. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ . Throughout the refinement individual isotropic temperature factors were used for each atom, since anisotropic refinement was clearly not justified by the data. The refined coordinates are given in Table I and the atom naming system in Figure 1. Standard deviations of position are 0.004 Å for Eu, 0.03 Å for the S atoms, 0.04–0.05 Å for the O atoms and 0.06–0.11 Å for the C and F atoms. The final observed and calculated values of the structure factors are available from the Editor upon request. The scattering factors used are those given in the International Tables,<sup>6</sup> that for Eu being corrected for anomalous dispersion.<sup>7</sup>

#### Discussion

##### Molecular Geometry

A perspective view of the molecule is shown in Figure 3. The geometry of the molecule is largely determined by the coordination of the Eu atom. The eight ligand atoms, two from each of the  $\beta$ -diketone groups and one from each of two water molecules, form an archimedean (or square) antiprism<sup>8</sup> as shown in Figure 2. The distance between the two square

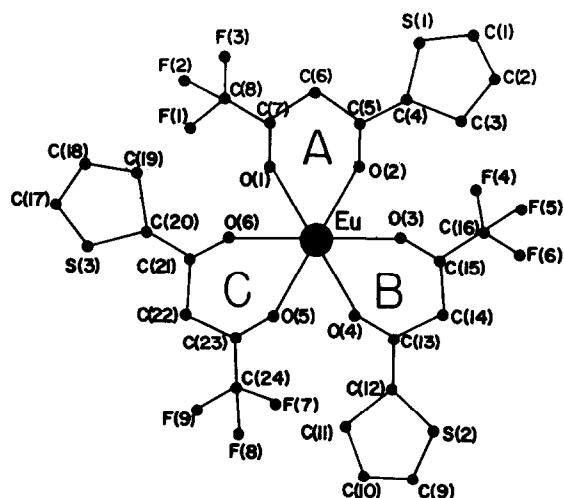


Figure 1. Numbering diagram of the molecule. The two coordinated water molecules not shown are designated O(7) and O(8).

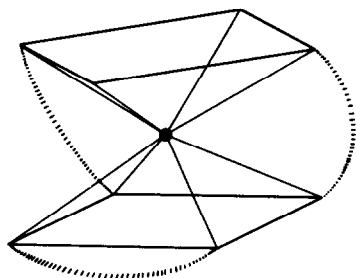


Figure 2. The archimedean antiprism of liganding oxygen atoms surrounding a europium atom. Each of the shaded lines connects two oxygen atoms of the same  $\beta$ -diketone group.

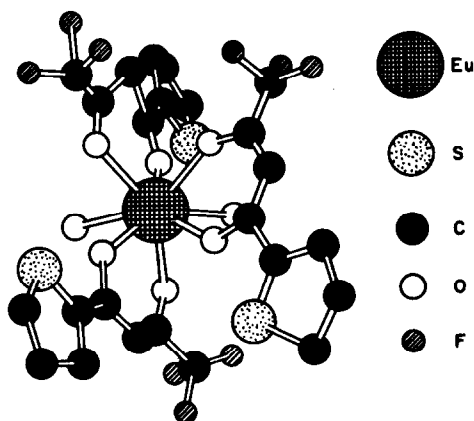


Figure 3. Perspective view of the molecule.

planes is smaller than a square edge so that the distances between oxygens of the same  $\beta$ -diketones are almost equal for all three groups (average 2.88(4) Å) as are the distances between the Eu atom and the eight O atoms. Since the antiprism may be considered to be formed from a cube by a relative rotation of 45° of one pair of opposite faces (plus a compression normal to the faces) intermediate rotations are possible. The accuracy of the description may therefore be tested by considering the 16 angles between the sides of the two squares. While individually some of these differ from 45° by as much as 8° the average systematic deviation, representing a clockwise rotation of the upper square in Figure 2, is only 2.3°. This is significant, however, since it is five times the standard deviation of the averaged measurement.

Groups A and B both have their ligands at corners of separate squares. In both these groups the six membered rings of the  $\beta$ -diketone and the Eu atom are far from planar being folded on the O—O line by 23° and 20° respectively. The equations of the mean planes for groups which are coplanar within experimental error are given in Table II. It can be seen that one consequence of the mode of liganding and of the Eu dihedral angles is that the  $\beta$ -diketones of A and B lie nearly in one great plane. In group C on the other hand, the  $\beta$ -diketone has both oxygens at adjacent corners of the same square and the Eu atom is coplanar with the other five atoms of the ring. This group is at 80° to the mean plane of the other two groups.

The bond distances in the molecular are not sufficiently accurate to discuss seriously. The data may be summarized by averaging all equivalent bonds. Bonds between like atoms on the two sides of the  $\beta$ -diketones while not strictly identical are indistinguishable and have been averaged together, as have the C—C bonds in the thienyl rings where the formal double and single bonds are not significantly different. Results are as follows: Eu—O (in the  $\beta$ -diketones), 2.42(2) Å; O—C, 1.27(4) Å; C—C (in the  $\beta$ -diketones), 1.42(5) Å; C—C ( $\beta$ -diketones to substituents), 1.52(5) Å; C—S, 1.71(4) Å; C—C (within the thienyl rings), 1.41(4) Å; C—F, 1.26(5) Å. The distances between the Eu atom and the oxygens of the two water molecules are measured as rather larger (2.53(4) Å) than the other Eu—O distances, but the difference is within the possible error and in any case the water molecules are firmly held in the coordination sphere. The O—O distances within each  $\beta$ -diketone average 2.88(4) Å, giving O—Eu—O angles (the 'bite' of the chelate) of 73(1)°.

The three thienyl groups are turned about the bonds C<sub>4</sub>—C<sub>5</sub> etc. such that each S atom is adjacent to the liganding O of the same group. The average S—O distance is 2.88(3) Å, considerably shorter than the sum of the van der Waals radii. This effect has been noted in many similar compounds<sup>2,3</sup> and has been explained

TABLE II. Parameters of the Least Squares Mean Planes in the Equation  $AX + BY + CZ = D$ . Coordinates are in Å Referred to Orthogonal Axes  $b$ ,  $c$  and Their Perpendicular.

Atoms	A	B	C	D
O(1)O(2)C(5)C(6)C(7)	0.243	0.203	0.949	1.789
O(3)O(4)C(13)C(14)C(15)	0.203	0.278	0.939	1.790
EuO(5)O(6)C(21)C(22)C(23)	0.970	-0.242	0.025	1.989
S(1)C(1)C(2)C(3)C(4)	0.432	0.254	0.866	2.583
S(2)C(9)C(10)C(11)C(12)	0.280	0.380	0.882	1.309
S(3)C(17)C(18)C(19)C(20)	0.985	-0.171	-0.013	1.515
O(1)O(4)O(5)O(6)	0.741	-0.403	-0.537	-0.895
O(2)O(3)O(7)O(8)	0.701	-0.404	-0.588	1.476

either as a specific S—O interaction or a forced compression of the van der Waals distance by repulsion of H atoms on the closest C atoms of the  $\beta$ -diketone and the thienyl ring.

#### Packing

A projection of several unit cells down the crystal  $b$  axis is shown in Figure 4. The full lines represent molecules where the Eu atoms have  $y = 0$ , while the dotted lines represent one molecule with Eu at  $y = 1/2$ .

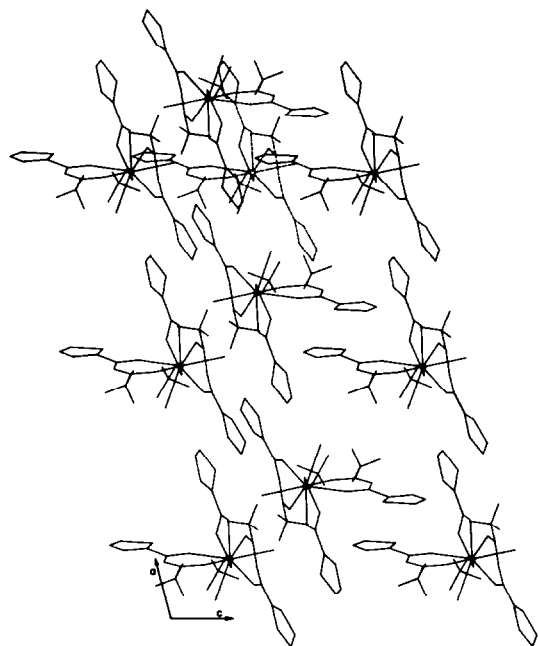


Figure 4. A view of several unit cells projected down the  $b$  axis. The full lines connect atoms in molecules with Eu atoms close to  $y = 0$ . The dotted outline is one molecule in the layer with Eu atoms close to  $y = 1/2$ .

Most of the intermolecular contacts are at normal van der Waals distances. However O(1) and O(4) in the standard molecule and the water molecule O(8) at  $-x, -y, -z$  are at distances of 2.9 and 3.0 Å respectively, and weak hydrogen bonding may exist. The shortest van der Waals approaches are between the atoms C(1) and C(2) of thienyl A in the standard molecule and the corresponding atoms of thienyl B in the molecule at  $-x, -y, -z$  (3.8 Å) and between F(5) of the standard molecule and F(3) of the molecule at  $-x, 1/2 + y, 1/2 - z$  (2.8 Å).

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