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Anhydrous tris(dibenzoylmethanido)(*o*-phenanthroline)europium(III), [Eu(DBM)$_3$(Phen)]

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Key indicators

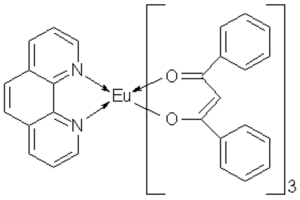
Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.007 Å
R factor = 0.050
wR factor = 0.094
Data-to-parameter ratio = 16.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The hydrated tris(dibenzoylmethanido)(*o*-phenanthroline)europium(III) complex, [Eu(DBM)$_3$(Phen)]$\cdot x$H$_2$O, is converted efficiently into anhydrous tris(dibenzoylmethanido)(*o*-phenanthroline)europium(III), [Eu(DBM)$_3$(Phen)] or [Eu(C$_{15}$H$_{11}$O$_2$)$_3$(C$_{12}$H$_8$N$_2$)], by heating under vacuum. The title compound has been characterized by FT–IR, ^{1}H and ^{13}C NMR spectroscopy, and X-ray diffraction methods. It crystallizes in the triclinic space group $P\overline{1}$ with five molecules in the asymmetric unit, without any pseudosymmetry. The trivalent europium ion is eight-coordinate, and the coordination polyhedron can best be described as a slightly distorted square antiprism.

Comment

There is much interest in the preparation of anhydrous europium β-diketonate complexes. These complexes have been extensively studied with respect to applications as NMR shift reagents (Briggs, 1970; Hinckley, 1969) and as laser materials (Whan & Crosby, 1962; Balzani, 1992; Qian *et al.*, 1997). More recently, lanthanides have attracted considerable attention for light-emitting diodes, because their photoluminescences (PL) exhibit high quantum efficiencies and very sharp spectral bands (Kido *et al.*, 1994; Sano *et al.*, 1995; Edwards *et al.*, 1997). Europium β-diketonate complexes have been well established in the literature for many years (Whan & Crosby, 1962; Pope *et al.*, 1961; Halverson *et al.*, 1964; Mazdiyasni *et al.*, 1966). Melby and co-workers have prepared a series of rare earth complexes and recorded their emission spectra (Melby *et al.*, 1964). However, most of these complexes are hydrated and contain inner coordinated water molecules, because their synthetic routes have generally used water-soluble salts, *e.g.* the hydrated tris(dibenzoylmethanido)(*o*-phenanthroline)europium(III), [Eu(DBM)$_3$(Phen)], has been prepared by using EuCl$_3\cdot$6H$_2$O. To the best of our knowledge, there were no published structural data or NMR studies of the anhydrous tris(dibenzoylmethanido)(*o*-phenanthroline)europium(III) complex. We report herein the solid-state structure of water-free [Eu(DBM)$_3$(Phen)], (I).



(I)

The structural features of complex (I) were identified on the basis of IR, and ^{1}H and ^{13}C NMR spectroscopy. The most

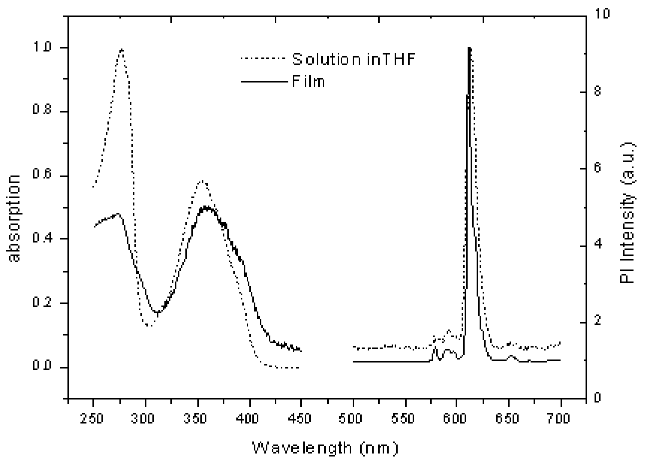


Figure 1
Absorption and emission spectra of complex (I): (···) absorption and emission in thf at room temperature and (—) absorption and emission in film.

notable feature in the IR spectrum of (I) is the absence of O—H stretching vibrations, indicating that there are no inner coordinated water molecules in the complex, which is in good agreement with the results of the elemental analysis and crystal structure. A well resolved ^{1}H NMR spectrum was observed for complex (I). The spectrum shows a single peak at δ 16.89 p.p.m. for the enolic proton of the dibenzoylmethane ligand, four single resonances at δ 8.92, 10.01, 10.52 and 10.92 p.p.m. corresponding to the phenanthroline protons, and a multiplet at δ 6.59–8.00 p.p.m. for the phenyl protons.

The absorption and PL spectra of complex (I), in a film formed by spin-coating directly on a quartz glass substrate (the spin-coating solution was 0.5wt% in chloroform), and in a THF solution at room temperature are shown in Fig. 1. Complex (I) has absorption and PL spectra nearly identical to the reported hydrated complex [Eu(DBM)$_3$(Phen)]$\cdot x$H$_2$O (Melby *et al.*, 1964). The complex exhibits an absorption peak at 356 nm, which can be assigned to the allowed π–π* transition of the β-diketone (DBM) ligand (Uekawa *et al.*, 1998). It can be seen that the PL spectra (excitation wavelength 356 nm) of the film and solution are very similar. They both exhibit four sharp emission peaks at 579, 591, 612 and 653 nm corresponding to the $^5D_0 \rightarrow ^7F_j$ (j = 0–3) transitions of the trivalent europium ion, respectively, in which the first, second and fourth peaks are weak and the third is the main peak. These emissions are a result of highly efficient intramolecular energy transfer from the ligand triplet state (which is generated by intersystem crossing from the singlet state of the ligand) to the excited state of the Eu^{3+} ion, $^5D_0$, which then relaxes to the ^7F_j (j = 0–3) states (Crosby & Whan, 1960; Bhaumik, 1965).

The title compound, (I), crystallizes in the space group $P\overline{1}$ with five crystallographically unrelated molecules in the asymmetric unit (Fig. 2). No pseudosymmetry is observed among the five molecules. The structure for one of the five crystallographically independent molecules is depicted in Fig. 3. The trivalent europium ion is eight-coordinate, and the coordination polyhedron can best be described as a slightly distorted square antiprism. The average Eu—O bond distances in the five molecules are almost equivalent [Eu(A)—O(A) 2.358 Å, Eu(B)—O(B) 2.354 Å, Eu(C)—O(C) 2.357 Å, Eu(D)—O(D) 2.357 Å and Eu(E)—O(E) 2.347 Å]; these bond distances are similar to the average Eu—O bond distances of 2.354 Å in tris(dibenzoylmethanido)(*o*-phenanthroline)europium(III) acetone solvate, [Eu(DBM)$_3$(Phen)]$\cdot$O(CH$_3$)$_2$ (Jian *et al.*, 1989), and 2.359 Å in tris(acetylacetone)-*o*-phenanthroline, [Eu(acac)$_3$(Phen)] (Watson *et al.*, 1972). The average Eu—N bond distance of 2.641 Å is comparable with the average Eu—N bond distance of 2.642 Å observed in [Eu(DBM)$_3$(Phen)]$\cdot$O(CH$_3$)$_2$ (Jian *et al.*, 1989). In the asymmetric unit, the molecules are held together by a number of weak C—H···O contacts (Table 2).

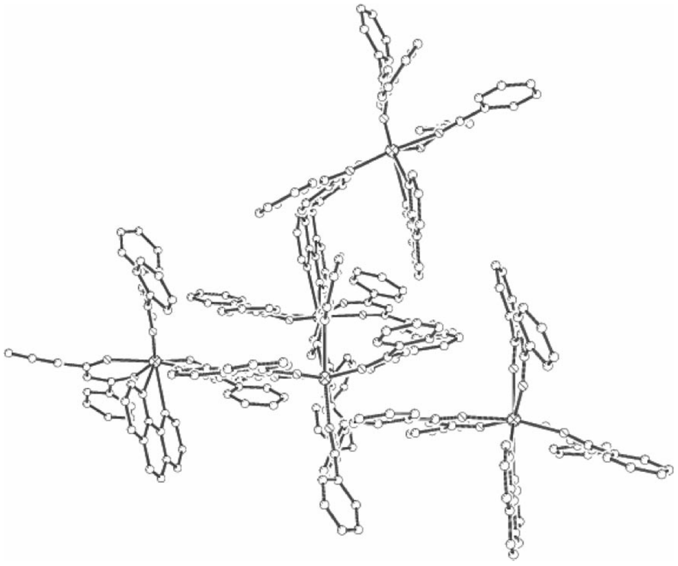


Figure 2
The asymmetric unit for complex (I), showing all five crystallographically independent molecules, excluding H atoms.

Experimental

The hydrated complex [Eu(DBM)$_3$(Phen)]$\cdot x$H$_2$O, was prepared by the method of Melby *et al.* (1964). The hydrated complex was transferred to a sublimation tube and heated to 433 K *in vacuo*, when all the water was driven off and the complex began to melt without decomposition. The temperature was raised to 453 K over a period of 12 h to melt the entire complex. The apparatus was cooled, and the molten product was dissolved in dichloromethane. After the solvent evaporated, the solid was washed five times with ethanol and dried under vacuum at room temperature for 12 h to give pure anhydrous [Eu(DBM)$_3$(Phen)]. Orange crystals of (I) were grown from an ethanol and dichloromethane solvent mixture by slow evaporation at room temperature. The purity of complex (I) was verified by elemental analysis: calculated for $C_{57}H_{41}EuN_2O_6$: C 68.30, H 4.10, N

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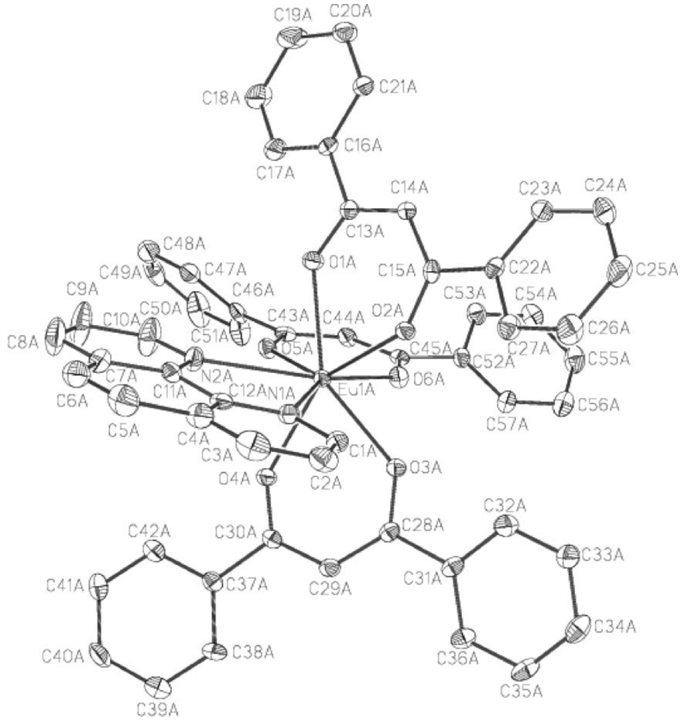

Figure 3

Representation of complex (I), with 30% probability displacement ellipsoids, for one of five crystallographically independent molecules. H atoms have been excluded for clarity.

2.80%; found: C 68.12, H 3.8, N 2.6% (m.p. 459–461 K). IR (neat) cm^{-1}: 1596, 1550, 1456, 724; ^{1}H NMR (CDCl$_3$): δ 6.59–8.00 (*m*, C$_6$H$_5$, 30 H), 8.92 (*s*, CH=, 2H), 10.01 (*s*, CH=, 2H), 10.52 (*s*, CH=, 2H), 10.92 (*s*, CH=, 2H), 16.89 (*s*, CH, 1H); ^{13}C NMR (CDCl$_3$): δ 109.7, 123.2–130.7, 131.9, 132.5, 135.5, 150.2, 168.5, 172.8, 180.5, 185.7.

Crystal data

[Eu(C$_{15}$H$_{11}$O$_2$)$_3$(C$_{12}$H$_8$N$_2$)]
M_r = 1001.88
Triclinic, $P\overline{1}$
a = 16.275 (6) Å
b = 23.504 (9) Å
c = 31.712 (12) Å
α = 103.844 (6)°
β = 91.466 (6)°
γ = 101.585 (6)°
V = 11504 (7) Å^3
Z = 10
D_x = 1.446 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1016 reflections
θ = 4.4–54.8°
μ = 1.42 mm^{-1}
T = 153 (2) K
Parallelepiped, yellow
0.24 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{\min}$ = 0.776, $T_{\max}$ = 0.868
102 650 measured reflections
49 686 independent reflections
32 004 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.061
$\theta_{\max}$ = 27.0°
$h = -20 \rightarrow 20$
$k = -30 \rightarrow 29$
$l = -36 \rightarrow 40$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.095
S = 0.99
49 686 reflections
2972 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.012
$\Delta\rho_{\max}$ = 0.61 e Å^{-3}
$\Delta\rho_{\min}$ = −0.68 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.000029 (6)

Table 1

Selected geometric parameters (Å, °).

Eu1*A*—O4*A*	2.312 (3)	O6*A*—C45*A*	1.278 (5)
Eu1*A*—O3*A*	2.339 (3)	C13*A*—C14*A*	1.408 (6)
Eu1*A*—O1*A*	2.351 (3)	C13*A*—C16*A*	1.513 (6)
Eu1*A*—O6*A*	2.354 (3)	C14*A*—C15*A*	1.401 (6)
Eu1*A*—O2*A*	2.382 (3)	C15*A*—C22*A*	1.506 (6)
Eu1*A*—O5*A*	2.413 (3)	C28*A*—C29*A*	1.385 (6)
Eu1*A*—N1*A*	2.651 (4)	C28*A*—C31*A*	1.498 (6)
Eu1*A*—N2*A*	2.661 (4)	C29*A*—C30*A*	1.406 (6)
O1*A*—C13*A*	1.267 (5)	C30*A*—C37*A*	1.503 (6)
O2*A*—C15*A*	1.272 (5)	C43*A*—C44*A*	1.406 (6)
O3*A*—C28*A*	1.291 (5)	C43*A*—C46*A*	1.483 (6)
O4*A*—C30*A*	1.272 (5)	C44*A*—C45*A*	1.398 (6)
O5*A*—C43*A*	1.272 (5)	C45*A*—C52*A*	1.494 (6)
O4*A*—Eu1*A*—O3*A*	71.83 (10)	C13*A*—O1*A*—Eu1*A*	137.8 (3)
O4*A*—Eu1*A*—O1*A*	145.26 (11)	C15*A*—O2*A*—Eu1*A*	137.9 (3)
O3*A*—Eu1*A*—O1*A*	142.83 (10)	C28*A*—O3*A*—Eu1*A*	135.3 (3)
O4*A*—Eu1*A*—O6*A*	102.09 (10)	C30*A*—O4*A*—Eu1*A*	136.8 (3)
O3*A*—Eu1*A*—O6*A*	75.14 (10)	C43*A*—O5*A*—Eu1*A*	135.9 (3)
O1*A*—Eu1*A*—O6*A*	92.87 (10)	C45*A*—O6*A*—Eu1*A*	137.4 (3)
O4*A*—Eu1*A*—O2*A*	139.52 (10)	O1*A*—C13*A*—C14*A*	123.9 (4)
O3*A*—Eu1*A*—O2*A*	74.83 (10)	O1*A*—C13*A*—C16*A*	115.0 (4)
O1*A*—Eu1*A*—O2*A*	70.21 (10)	C14*A*—C13*A*—C16*A*	121.1 (4)
O6*A*—Eu1*A*—O2*A*	90.76 (10)	C15*A*—C14*A*—C13*A*	123.5 (4)
O4*A*—Eu1*A*—O5*A*	81.57 (10)	O2*A*—C15*A*—C14*A*	123.7 (4)
O3*A*—Eu1*A*—O5*A*	131.45 (11)	O2*A*—C15*A*—C22*A*	116.5 (4)
O1*A*—Eu1*A*—O5*A*	73.60 (10)	C14*A*—C15*A*—C22*A*	119.8 (4)
O6*A*—Eu1*A*—O5*A*	71.68 (11)	O3*A*—C28*A*—C29*A*	123.6 (4)
O2*A*—Eu1*A*—O5*A*	138.69 (9)	O3*A*—C28*A*—C31*A*	114.9 (4)
O4*A*—Eu1*A*—N1*A*	79.84 (11)	C29*A*—C28*A*—C31*A*	121.4 (4)
O3*A*—Eu1*A*—N1*A*	76.26 (11)	C28*A*—C29*A*—C30*A*	124.2 (4)
O1*A*—Eu1*A*—N1*A*	102.90 (11)	O4*A*—C30*A*—C29*A*	123.8 (4)
O6*A*—Eu1*A*—N1*A*	149.03 (12)	O4*A*—C30*A*—C37*A*	115.4 (4)
O2*A*—Eu1*A*—N1*A*	70.40 (10)	C29*A*—C30*A*—C37*A*	120.8 (4)
O5*A*—Eu1*A*—N1*A*	138.23 (11)	O5*A*—C43*A*—C44*A*	124.3 (4)
O4*A*—Eu1*A*—N2*A*	73.72 (11)	O5*A*—C43*A*—C46*A*	118.4 (4)
O3*A*—Eu1*A*—N2*A*	129.17 (10)	C44*A*—C43*A*—C46*A*	117.3 (4)
O1*A*—Eu1*A*—N2*A*	77.34 (11)	C45*A*—C44*A*—C43*A*	125.0 (4)
O6*A*—Eu1*A*—N2*A*	148.95 (12)	O6*A*—C45*A*—C44*A*	124.5 (4)
O2*A*—Eu1*A*—N2*A*	112.64 (12)	O6*A*—C45*A*—C52*A*	116.4 (4)
O5*A*—Eu1*A*—N2*A*	77.29 (12)	C44*A*—C45*A*—C52*A*	119.0 (4)
N1*A*—Eu1*A*—N2*A*	61.69 (12)	C43*B*—C44*B*—C45*B*	123.5 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1*A*—H1A*A*···O3*A*	0.95	2.54	3.119 (6)	120
C10*A*—H10*A*···O5*A*	0.95	2.40	3.094 (8)	129
C10*B*—H10*B*···O5*B*	0.95	2.44	2.997 (6)	118
C10*C*—H10*C*···O3*C*	0.95	2.38	3.016 (6)	124
C10*D*—H10*D*···O3*D*	0.95	2.42	3.017 (6)	121
C10*E*—H10*E*···O3*E*	0.95	2.51	3.153 (6)	125
C17*A*—H17*A*···O1*A*	0.95	2.38	2.716 (6)	100
C32*B*—H32*B*···O3*B*	0.95	2.40	2.736 (7)	100
C47*C*—H47*C*···O5*C*	0.95	2.36	2.702 (6)	100
C47*E*—H47*E*···O5*E*	0.95	2.32	2.679 (6)	101
C53*E*—H53*E*···O6*E*	0.95	2.36	2.692 (6)	100
C57*C*—H57*C*···O6*C*	0.95	2.40	2.730 (7)	100

All H atoms were placed geometrically and refined using a riding model with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) and C—H = 0.95 Å. Atoms C55C and C56C have slightly large displacement parameters. A disorder model with two orientations for the phenyl ring did not improve the refinement.

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Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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