

# SYNTHESIS AND CHARACTERIZATION OF TRIS(3-PHENYL-4-BENZOYL-5-ISOXAZOLONE) (1,10-PHENANTHROLINE)EUROPIUM

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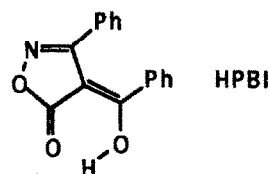
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**Abstract**—Europium trichloride reacted with HPBI and O-phen to give  $\text{Eu}(\text{PBI})_3(\text{O-phen})$ , crystallization of which in  $\text{CHCl}_3$ -EtOH yielded yellow crystals. X-ray analysis showed that the europium is coordinated to two nitrogen atoms of the O-phen and six oxygen atoms of the three PBI ligands. The eight donating atoms form a square antiprism around the central europium atom.

$\beta$ -Diketones have received extensive attention as lanthanide extractants in solvent extraction.<sup>1-3</sup> The acidity of the extractant is an important factor in the extraction process. 3-Phenyl-4-benzoyl-5-isoxazolone (HPBI) is strongly acidic compared with most other  $\beta$ -diketones, including the widely used 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP),<sup>4</sup> and thus can extract metals from more acidic regions. The reagent HPBI has been used earlier in the study of extraction of transition metals such as Cd, Pb and Rh.<sup>5</sup> Umetani *et al.* recently found HPBI to be a very powerful lanthanide extractant.<sup>6</sup> Bangroo *et al.* also studied the extraction of erbium with HPBI.<sup>7</sup> However, the composition of the complex formed in the extraction process is still not well defined, and molecular structures containing the HPBI ligand are unknown. In this paper we report the synthesis and crystal structure of the title complex  $\text{Eu}(\text{PBI})_3(\text{O-phen})$ .



## EXPERIMENTAL

### Preparation of $\text{Eu}(\text{PBI})_3(\text{O-phen})$

Europium oxide  $\text{Eu}_2\text{O}_3$  (46 mg) was dissolved in excess concentrated HCl, the solvent  $\text{H}_2\text{O}$  was carefully evaporated on a hot plate and the residue was then dissolved in 2 cm<sup>3</sup> absolute ethanol to give a  $\text{EuCl}_3$  ethanol solution. HPBI (206 mg) and 1,10-phenanthroline (53 mg) were dissolved in 8 cm<sup>3</sup> absolute ethanol and mixed with the  $\text{EuCl}_3$  solution. The pH of the resulting mixture was adjusted to ca 4 by adding NaOH (5 M) dropwise. The solvent was evaporated on a rotary evaporator, and the residue was extracted with 10 cm<sup>3</sup>  $\text{CHCl}_3$ . The

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Table 1. Selected bond lengths (Å)

Eu—O(1)	2.363(4)	Eu—O(7)	2.368(4)
Eu—O(3)	2.386(4)	Eu—O(9)	2.387(4)
Eu—O(4)	2.333(5)	Eu—N(4)	2.551(5)
Eu—O(6)	2.400(4)	Eu—N(5)	2.557(4)

CHCl<sub>3</sub> was filtered and concentrated to about 2 cm<sup>3</sup>, then 4 cm<sup>3</sup> absolute ethanol and 1 cm<sup>3</sup> H<sub>2</sub>O were added. The solution was allowed to evaporate slowly in air to give pale yellow crystals of Eu(PBI)<sub>3</sub>(O-phen).

#### X-ray analysis

A crystal having approximate dimensions of 0.1 × 0.1 × 0.25 mm<sup>3</sup> was mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromator with Mo-K<sub>α</sub> radiation. A total of 8541 independent reflections were collected in the range 2° ≤ θ ≤ 23° by the ω-2θ scan technique at room temperature, of which 3628 with [I ≥ 3σ(I)] were considered to be observed and used in the refinement. A correction for Lorentz and polarization effects was applied to the data.

The structure was solved by direct methods (MULTAN 82). The europium was located on an E-map. All the non-hydrogen atoms were determined from successive difference Fourier syntheses. The final refinement by full-matrix least-squares with anisotropic thermal parameters for non-hydrogen atoms converged to *R* and *R<sub>w</sub>* factors of 0.046 and 0.053, respectively. The highest peak on the final difference Fourier map had a height of 0.99 e Å<sup>-3</sup>. In the final refinement process, the occupancy of the solvent molecule CHCl<sub>3</sub> was set at 0.5 and reasonable thermal parameters were obtained for its non-hydrogen atoms.

#### Crystal data

[C<sub>60</sub>H<sub>38</sub>N<sub>5</sub>O<sub>9</sub>Eu] 0.5[CHCl<sub>3</sub>], F.W. = 1184.6, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 16.676(3), *b* = 10.671(3), *c* = 32.243(8) Å, β = 97.65(1)°, *V* = 5686 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.38 g cm<sup>-3</sup>, *F*(000) = 2475.

All calculations were performed on a PDP 11/44 computer using the SDP-PLUS program system.

## RESULTS AND DISCUSSION

The complex Eu(PBI)<sub>3</sub>(O-phen) is mononuclear, as expected. The europium atom is coordinated to

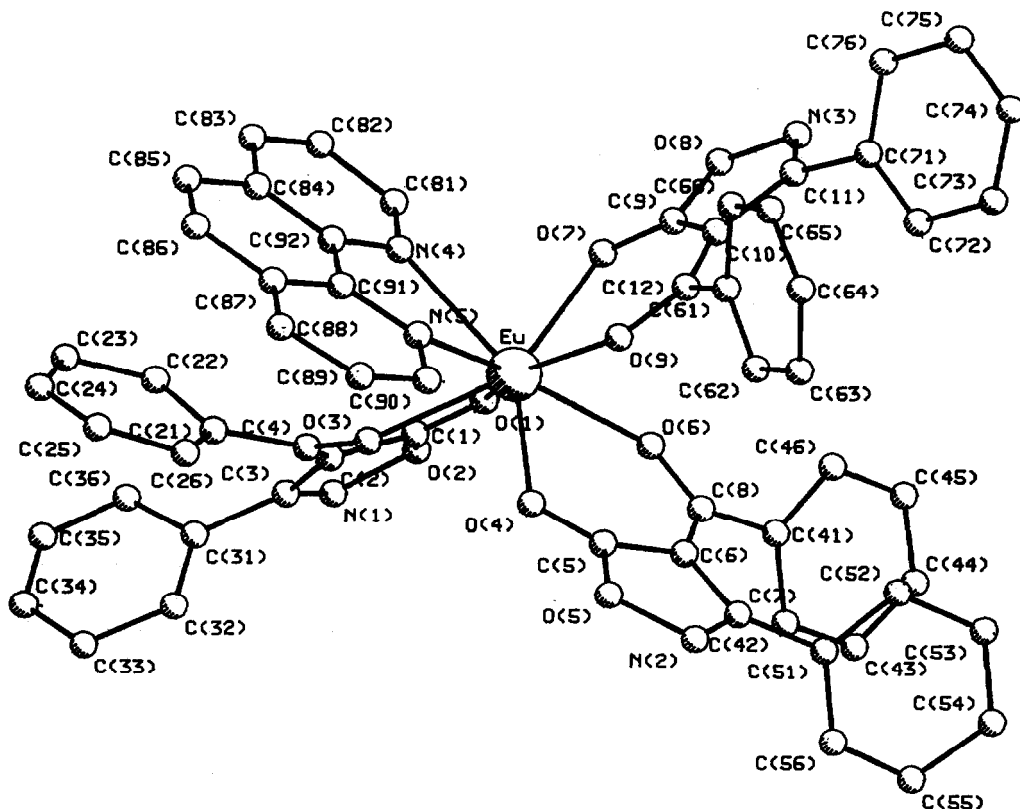


Table 2. Selected bond angles ( $^{\circ}$ )

O(1)—Eu—O(3)	73.3(1)	O(4)—Eu—O(7)	139.4(1)
O(1)—Eu—O(4)	114.6(1)	O(4)—Eu—O(9)	74.0(1)
O(1)—Eu—O(6)	76.7(1)	O(4)—Eu—N(4)	138.7(2)
O(1)—Eu—O(7)	85.1(1)	O(4)—Eu—N(5)	79.1(2)
O(1)—Eu—O(9)	149.9(1)	O(6)—Eu—O(7)	77.1(1)
O(1)—Eu—N(4)	83.0(1)	O(6)—Eu—O(9)	78.5(1)
O(1)—Eu—N(5)	135.2(1)	O(6)—Eu—N(4)	147.1(1)
O(3)—Eu—O(4)	77.2(1)	O(6)—Eu—N(5)	145.7(1)
O(3)—Eu—O(6)	123.9(1)	O(7)—Eu—O(9)	72.8(1)
O(3)—Eu—O(7)	143.3(1)	O(7)—Eu—N(4)	75.6(1)
O(3)—Eu—O(9)	135.9(1)	O(7)—Eu—N(5)	112.6(1)
O(3)—Eu—N(4)	72.7(1)	O(9)—Eu—N(4)	110.0(1)
O(3)—Eu—N(5)	68.6(1)	O(9)—Eu—N(5)	73.7(1)
O(4)—Eu—O(6)	74.0(1)	N(4)—Eu—N(5)	64.0(2)

two nitrogen atoms of the 1,10-phenanthroline and six oxygen atoms of the three 3-phenyl-4-benzoyl-5-isoxazolone ligands. The eight coordinating atoms form a square antiprism. Plane 1 of the square antiprism consists of N(4), N(5), O(7) and O(9); plane 2 consists of O(1), O(3), O(4) and O(6). The two planes are almost parallel with a  $4.8^{\circ}$  dihedral angle. The europium is 1.38 Å from plane 1 and 1.19 Å from plane 2. The average Eu—O bond distance is 2.37 Å, slightly shorter than the Eu—N distance, 2.55 Å (Table 1). The average distance between the two donating oxygen atoms of the diketone is 2.84 Å close to the calculated value of 2.9 Å.<sup>6</sup>

All the five-membered rings are planar. The dihedral angle between the five-membered rings and the phenyl groups is far from the ideal  $90^{\circ}$ , ranging from  $53^{\circ}$  to  $61^{\circ}$  (Table 2). The two phenyl groups on the same PBI ligand are face to face but not parallel, and their dihedral angle varies from  $26^{\circ}$  to  $47^{\circ}$ . This deviation from the ideal configuration may be a result of the weak conjugation throughout the entire ligand.<sup>8</sup>

The IR spectrum of the HPBI ligand shows two strong C=O stretching bands at 1618 and 1697  $\text{cm}^{-1}$ , typical for the keto-enol tautomerism of  $\beta$ -diketones, and several other medium intensity

bands in the range from 697 to 1595  $\text{cm}^{-1}$ . In comparison, the IR spectrum of the complex  $\text{Eu}(\text{PBI})_3(\text{O-phen})$  looks much simpler. There is only one strong C=O stretching band at 1641  $\text{cm}^{-1}$ , two medium intensity bands at 1501 and 1483  $\text{cm}^{-1}$  and several very weak bands in the range from 658 to 1602  $\text{cm}^{-1}$ .

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