

Note

Crystal Structure of Complex Tris(4,4,4-trifluoro-1-phenyl-1,3-butanedione)(1,10-phenanthroline) Europium(III)

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The complex $\text{Eu}(\text{btfa})_3(\text{phen})$ (btfa = 4,4,4-trifluoro-1-phenyl-1,3-butanedione, phen = 1,10-phenanthroline) has been prepared and characterized by elemental analysis, IR and UV spectroscopies. The crystal and molecular structures of the complex have been determined by X-ray diffraction analysis. It belongs to the monoclinic crystal system, space group $P2_1/c$ with $a = 0.9700(2)$ nm, $b = 3.7450(5)$ nm, $c = 1.0917(3)$ nm, $\beta = 92.51(2)^\circ$, $V = 3.962(1)$ nm³, $Z = 4$, $D_c = 1.639$ g/cm³, $\mu = 1.676$ mm⁻¹, $F(000) = 1936$, $R_1 = 0.0388$, $wR_2 = 0.0775$. Structure analysis shows that the europium(III) ion is coordinated to six oxygen atoms of β -diketonate anions and two nitrogen atoms of phenanthroline molecule. The coordination polyhedron is an approximate square antiprism.

Keywords europium(III) complex, benzoyltrifluoroacetone, 1,10-phenanthroline, crystal structure

Introduction

Certain lanthanide ions possess sharp emission lines in the visible regions. The possibility of transferring energy efficiently to these ions by way of strongly absorbing transitions characteristic of organic ligands has spurred many workers to investigate lanthanide chelates as potential laser materials. Among them the ternary complexes of europium(III) and terbium(III) with tris(β -diketonates) and an neutral ligand have especially attracted much attention for their strong luminescence. It makes them have extensive applications in development of new luminescence materials, probing the structures of biomacromolecules and in immunofluorescent test. The neutral ligands that can form adducts with the tris- β -diketonates include heterocyclic nitrogen donors such as pyridine, 2,2-dipyridyl and 1,10-phenanthroline as well as oxygen donors such as triphenylphosphine oxide, pyridine-*N*-oxide and 1,10-phenanthroline-*N*-oxide. The complex tris(4,4,4-trifluoro-1-phenyl-1,3-butanedione)(1,10-phenanthroline) europium(III) was first reported by Herbert *et al.*¹ Since its luminescence is very strong, the luminescence spectra of this complex have been characterized extensively in the solid state, organic solution and aqueous solution.¹⁻⁴ As far as we

know, any report on the molecular and crystal structures of this complex is not available. In this paper, the crystal structure of this ternary complex, $\text{Eu}(\text{btfa})_3(\text{phen})$ (btfa = 4,4,4-trifluoro-1-phenyl-1,3-butanedione, phen = 1,10-phenanthroline), and its spectroscopic characterizations are reported.

Results and discussion

The IR study shows that the band at 1603 cm⁻¹ in free ligand Hbtfa can be assigned to the stretching mode $\nu(\text{C}=\text{O})$ which is lower than that of the normal carbonyl. This may be attributed to the enol structure along with an intramolecular hydrogen bond in the β -diketone. The extensive conjugation weakened the C=O bond considerably.⁶ Compared with the $\nu(\text{C}=\text{O})$ band in free Hbtfa, the band in the complex is shifted to a higher frequency at 1613 cm⁻¹. It indicates that the conjugation extent is reduced after the coordination bond between oxygen atoms and Eu(III) ion is formed. For the ligand 1,10-phenanthroline the band at 1517 cm⁻¹ assigned to $\nu(\text{C}=\text{N})$ is shifted to 1488 cm⁻¹ ($\Delta\nu = -29$ cm⁻¹), indicating that the nitrogen atoms strongly coordinated to Eu(III) ion. The UV spectra of the complex display three main absorption bands. They are characterized by the ligands Hbtfa and phen. The absorption bands of the complex at 230 and 263 nm are assigned to the transition $\pi \rightarrow \pi^*$ of pyridine and benzene rings, respectively. The absorption band at 324 nm is assigned to the transition $\pi \rightarrow \pi^*$ of the conjugation system in btfa. Compared with free ligands, a significant increase in intensity of the corresponding bands appeared in the complex.

The fluorescence data for the title complex are listed in Table 1 and the fluorescence spectrum is shown in Fig. 1. The emission intensity mainly arises from $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. Although the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions also have some contributions, they are one-24th and one-18th of that of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ in intensity, respectively. This result is consistent with the other report.³

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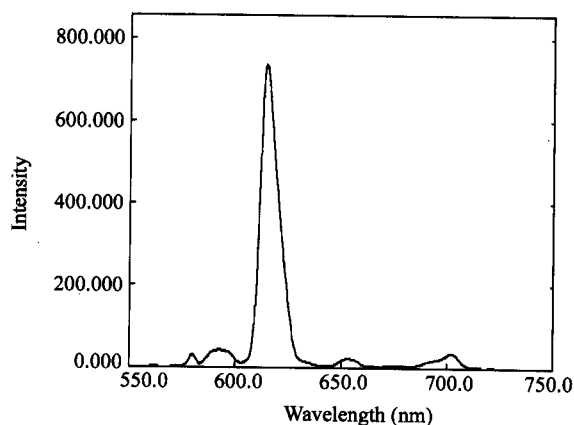


Fig. 1 Luminescence spectrum of the complex (in methanol).

Table 1 Luminescence data for the complex ($\lambda_{exc} = 355.0$ nm, in methanol)

S_1	5D_0				
S_2	7F_0	7F_1	7F_2	7F_3	7F_4
λ_{em} (nm)	580.0	592.0	614.0	653.0	702.0
I	30.80	41.32	735.2	23.01	35.07

$\text{Eu}(\text{btfa})_3(\text{phen})$ exists in the crystalline state as neutral monomeric molecule. The molecular structure, the molecular packing arrangement in the unit cell and the coordination polyhedron of europium(III) ion are shown in Figs. 2, 3 and 4, respectively. As expected, the europium(III) ion is eight-coordinated to all six β -diketone oxygen atoms and the two nitrogen atoms from the 1,10-phen. The coordination polyhedron is a slightly distorted square antiprism. The distances of C—O bonds in the coordinated btfa are 0.1250(7), 0.1270(7), 0.1260(6), 0.1251(6), 0.1258(6), 0.1264(6)

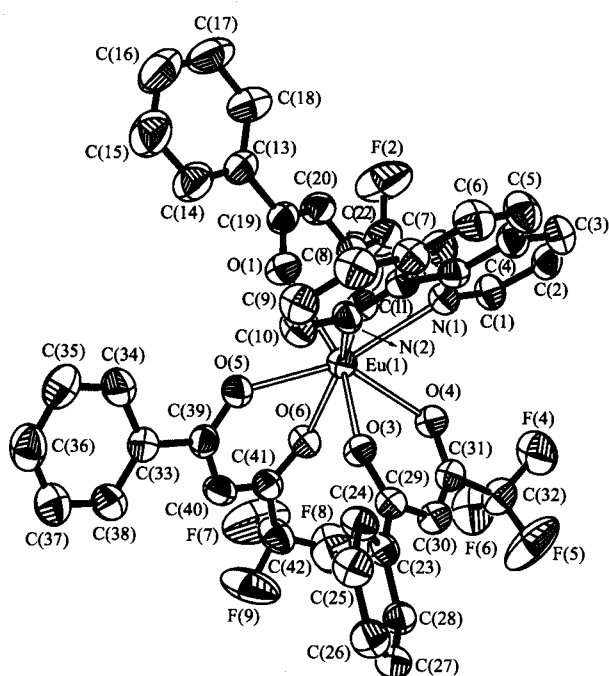


Fig. 2 Molecular structure of the title complex.

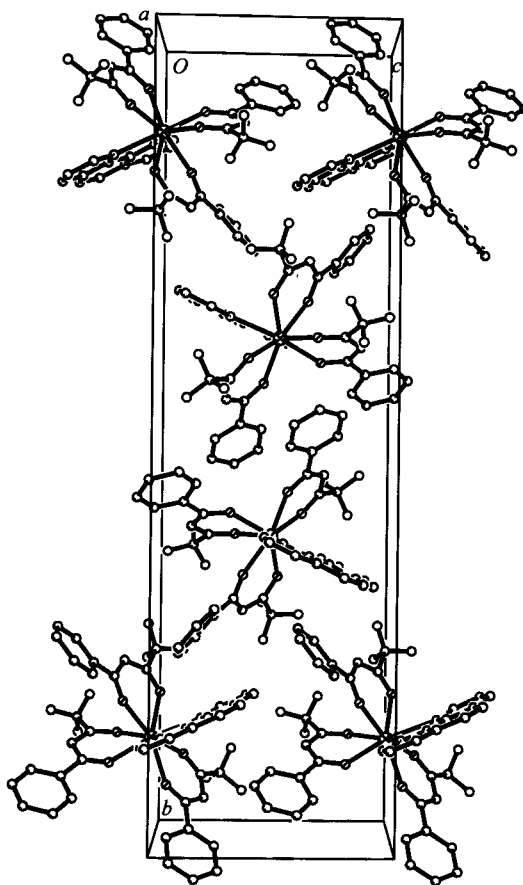


Fig. 3 Molecular packing arrangement in a unit cell of the title complex.

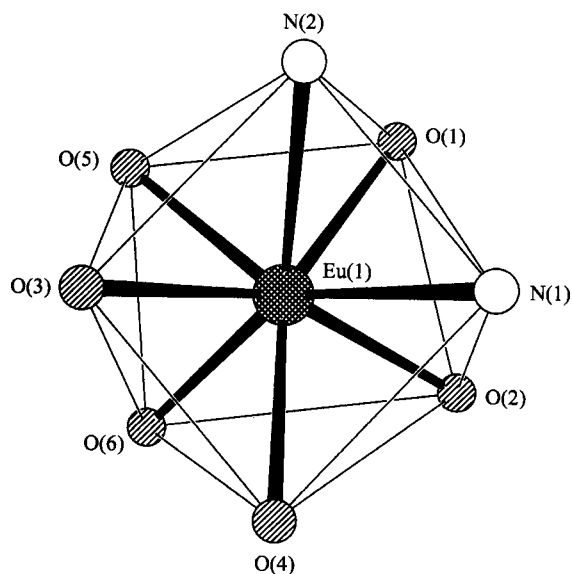


Fig. 4 Coordination polyhedron of europium(III) ion.

nm, respectively. The average of the C—O bond distances is 0.1259 nm, a little longer than that of normal C=O (0.1220 nm). The distances of C(19)—C(20), C(20)—C(21), C(29)—C(30), C(30)—C(31), C(39)—C(40), C(40)—C(41) of the coordinated btfa are 0.1417(8), 0.1356(8), 0.1415(7), 0.1373(7), 0.1408(8), 0.1373(8) nm, re-

spectively. The average of the C—C bond distances is 0.1390 nm, very close to that of the C—C bond (0.1397 nm) in benzene ring. All these indicated that the acyclic chain of btfa expectedly exhibited an extensive conjugation, when coordinated to Eu(III) ion. N(1), N(2), O(3), O(4) form one of the square faces. O(1), O(2), O(6), O(5) form the other. The average Eu—O distance of 0.2372(4) nm and average Eu—N distance of 0.2596(4) nm are typical for complexes of this type.⁷ The distances of C(13)—C(19), C(23)—C(29), C(33)—C(39) are 0.1490(8), 0.1496(7), 0.1502(8) nm, respectively, which are close to normal C—C bond (Table 2). It indicates that the β -diketones do not conjugate with benzoyl group of btfa in the complex.

Experimental

4,4,4-Trifluoro-1-phenyl-1,3-butanedione was purchased from Aldrich. The other chemicals were of reagent grade, and used without further purification. The europium (III) content was determined by EDTA titration. C, H and N were determined using a Perkin-Elmer 240C elemental analyzer. UV spectra were measured on a WFZ-900-D4 spectrophotometer in methanol solution. IR spectra were recorded on a Nicolet 7199B FT-IR spectrometer with KBr pellets in the 400—4000 cm^{-1} region. Luminescence spectrum was recorded on a RF-5301PC luminescence spectrometer in methanol solution.

Preparation of the complex

A stoichiometric quantity of btfa in ethanol was added to an ethanolic solution of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$. The pH of mixed solution was adjusted to 6.1 with NaOH aqueous solution. The liquor was slightly turbid and then filtered. An acetone solution of 1,10-phenanthroline was added to the filtrate dropwise with stirring. The reacting solution was filtered after refluxed with stirring for 7 h. After the filtrate was standing at room temperature for 3 days, the product was isolated as pale pink precipitate, washed with ethanol-acetone (1:1). The precipitate

was recrystallized in acetonitrile and some pale yellow crystals which are suitable for X-ray crystal analysis were obtained after 3 weeks. The crystals were characterized to have a formula of $\text{C}_{42}\text{H}_{26}\text{F}_9\text{N}_2\text{O}_6\text{Eu}$ ($M_r = 977.61$). Anal. calcd for C 51.60, H 2.68, N 2.87, Eu 15.54; found C 51.25, H 2.50, N 3.09, Eu 15.50.

The complex is soluble in many organic solvents, such as DMSO, CHCl_3 , CH_3CN , CH_3OH , but insoluble in water. The melting point is 179—182 °C.

X-Ray structural determination of the complex

A yellow block crystal with a dimension of 0.2 mm \times 0.2 mm \times 0.3 mm was mounted on a glass fiber. All measurements were made on a Bruker P4 diffractometer equipped with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071073$ nm) at (295 ± 2) K. Unit cell was obtained and refined using 36 well centered reflections with $5.0^\circ < \theta < 12.7^\circ$. Data collection was monitored by three standards every 100 reflection collected. No decay was observed except the statistic fluctuation in the range of $\pm 6.5\%$. Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical method based on Ψ -scan data. Direct phase determination yielded the positions of Eu, O, N and the most C and F atoms, and the other C and F atoms were located in successive difference Fourier syntheses. Hydrogen atoms were generated theoretically and fixed on their parent atoms in the final refinement. All non-hydrogen atoms were subjected to anisotropic refinement. The final full-matrix least-square refinement on F^2 converged at $R_1 = 0.0388$ and $wR_2 = 0.0775$ for 4498 observed reflections [$I \geq 2\sigma(I)$]. The final difference electron density map shows no features. Data collection was controlled by XSCANS program. Computations were performed using the SHELXTL NT ver. 5.10 program package on a IBM PC 586 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.⁵ Crystal drawing were produced with XP. The crystal data and structure refinement is given in Table 3. Selected bond lengths and angles are given in Table 2.

Table 2 Selected bond lengths (nm) and bond angles (°)

Eu(1)—O(6)	0.2358(4)	Eu(1)—N(1)	0.2607(4)
Eu(1)—O(1)	0.2359(4)	Eu(1)—N(2)	0.2585(4)
Eu(1)—O(5)	0.2364(4)	C(13)—C(19)	0.1490(8)
Eu(1)—O(2)	0.2364(4)	C(23)—C(29)	0.1496(7)
Eu(1)—O(3)	0.2372(4)	C(33)—C(39)	0.1502(8)
Eu(1)—O(4)	0.2413(4)		
O(1)—C(19)	1.250(7)	C(19)—C(20)	1.417(8)
O(2)—C(21)	1.270(7)	C(20)—C(21)	1.356(8)
O(3)—C(29)	1.260(6)	C(29)—C(30)	1.415(7)
O(4)—C(31)	1.251(6)	C(30)—C(31)	1.373(7)
O(5)—C(39)	1.258(6)	C(39)—C(40)	1.408(8)
O(6)—C(41)	1.264(6)	C(40)—C(41)	1.373(8)

Continued

O(6)-Eu(1)-O(1)	117.96(14)	O(6)-Eu(1)-O(3)	82.93(13)
O(6)-Eu(1)-O(5)	71.57(13)	O(1)-Eu(1)-O(3)	134.26(13)
O(1)-Eu(1)-O(5)	73.58(14)	O(5)-Eu(1)-O(3)	76.29(13)
O(6)-Eu(1)-O(2)	88.38(13)	O(2)-Eu(1)-O(3)	153.93(13)
O(1)-Eu(1)-O(2)	71.24(13)	O(6)-Eu(1)-O(4)	73.28(13)
O(5)-Eu(1)-O(2)	123.98(14)	O(1)-Eu(1)-O(4)	151.01(13)
O(5)-Eu(1)-O(4)	134.07(13)	O(4)-Eu(1)-N(1)	72.07(13)
O(2)-Eu(1)-O(4)	83.10(13)	N(2)-Eu(1)-N(1)	62.95(13)
O(3)-Eu(1)-O(4)	70.87(12)	C(19)-O(1)-Eu(1)	139.0(4)
O(6)-Eu(1)-N(2)	145.69(13)	C(21)-O(2)-Eu(1)	132.8(4)
O(1)-Eu(1)-N(2)	71.34(14)	C(29)-O(3)-Eu(1)	139.1(3)
O(5)-Eu(1)-N(2)	81.01(13)	C(31)-O(4)-Eu(1)	131.9(3)
O(2)-Eu(1)-N(2)	124.67(13)	C(39)-O(5)-Eu(1)	134.9(4)
O(3)-Eu(1)-N(2)	70.60(13)	C(41)-O(6)-Eu(1)	129.3(3)
O(4)-Eu(1)-N(2)	115.67(13)	C(1)-N(1)-C(12)	117.5(5)
O(6)-Eu(1)-N(1)	143.69(13)	C(1)-N(1)-Eu(1)	121.8(4)
O(1)-Eu(1)-N(1)	88.83(14)	C(12)-N(1)-Eu(1)	120.5(3)
O(5)-Eu(1)-N(1)	143.51(13)	C(10)-N(2)-C(11)	116.3(5)
O(2)-Eu(1)-N(1)	77.06(13)	C(10)-N(2)-Eu(1)	122.5(4)
O(3)-Eu(1)-N(1)	95.69(13)	C(11)-N(2)-Eu(1)	121.1(3)

Table 3 Crystal data and structure refinement

Molecular formula	C ₄₂ H ₂₆ F ₉ N ₂ O ₆ Eu
Molecular weight	977.61
Color and habit	Yellow block
Crystal size	0.2 mm × 0.2 mm × 0.3 mm
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
Unit cell parameters	<i>a</i> = 0.97004(15) nm <i>b</i> = 3.7450(5) nm, <i>β</i> = 92.513(15)° <i>c</i> = 1.0917(3) nm
Volume, <i>Z</i>	3.9621(13) nm ³ , 4
<i>F</i> (000)	1936
Density (calcd)	1.639 g/cm ³
Diffractometer	Bruker P4
Radiation	Graphite-monochromatized Mo K α , λ = 0.071073 nm
Temperature	(295 ± 2) K
Scan type	Ψ -scan
Data collection range	0 < <i>h</i> < 11, -44 < <i>k</i> < 0, -12 < <i>l</i> < 12; θ_{\max} = 25°
Reflections measured	Total: 7257 Unique (<i>n</i>): 6796 Observed [<i>I</i> ≥ 2 σ (<i>I</i>): 4498
Absorption coefficient	1.676 mm ⁻¹
Minimum and maximum transmission	0.23868, 0.29025
No. of variables, <i>p</i>	542
<i>R</i> ₁ ^a	0.0703 (for all reflections) 0.0388 (for observed data)
<i>wR</i> ₂ ^a	0.0946 (for all reflections) 0.0775 (for observed data)
Goof ^a	1.062
Largest and mean Δ/σ	0.001, 0.000
Residual extrema in final difference map	-388 to 701 e/nm ³

$$^a R_1 = \frac{\sum \|F_o - |F_c|\|}{\sum |F_o|}, wR_2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2}}, \text{Goof} = S = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{n - p}}$$

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