

Syntheses, Crystal Structure and Photoluminescence Properties of Piperidinium Tetrakis (1,3-Diphenyl-1,3-Propanedionato) Europate(III) Complex and Its Two Different Crystals

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Abstract

Treatment of 1,3-diphenyl-1,3-propanedione **1a** with europium (III) chloride in the presence of piperidine results in the halide ligands exchange giving newly piperidinium tetrakis (1,3-diphenyl-1,3-propanedionato)europate(III) complex **2a**. The complex was characterized by ¹H-NMR, positive FAB-mass, and Elemental Analysis. The exact molecular structure of **2a** was determined by single crystal X-ray diffraction with the monoclinic space group *Cc* (centrosymmetric, No.13). The large cavity sizes of the complex **2a** facilitated the inclusion of water and benzene solvate molecules. The other two different crystals **2b**, **2c** having two water molecules and one benzene molecule were obtained by the crystallization in different solvents and the exact molecular structures were determined by single crystal X-ray diffraction analysis with space groups *P2₁/n* (centrosymmetric, No.14), and *P2₁/n* (centrosymmetric, No.14), respectively. The eight coordinate structures of the complexes in the three crystals were slightly different due to the crystal packing and the existence of the solvent molecule(s). The photoluminescence studies indicated that four β -diketone ligands acted as strong antenna ligands and transferred the absorbed energy to europium (III) ion, consequently red luminescence was observed. These strong emissions were attributed to the ⁵D₀ → ⁷F₂ transition of Europium (III) ions under UV excitation. The photoluminescence spectrum of the three crystals was almost same in solid as well as in solution.

Keywords

Tetrakis Europium Complexes, Luminescence, β -Diketone Ligands

1. Introduction

The luminescent properties europium complexes have been of great interest because of their high luminescence emission efficiency, long fluorescence life time, large Stokes shift, sharp emission bands [1] [2] [3]. Therefore, various europium complexes with various organic ligands have been investigated for decades and still the search for novel europium complexes has been attracting many researchers due to the important applications of these complexes as optical fiber lasers, electroluminescent displays and organic light emitting diodes [4] [5] [6]. On the other hand, β -diketones as organic ligands have been attracted great attention because of their high complexing ability due to O,O-donor ligands, which are widely used in co-ordination transition metals [7]. Among these, Europium (III) complexes with β -diketones possessing aromatics substituents displayed very good to excellent photo luminescent properties. Thus, various Europium (III) complexes with β -diketones were synthesized and evaluated for their photo luminescent properties [8] [9] [10] [11] [12].

In this context, we report the synthesis, structural and spectral properties of the octa-coordinate Europium (III) complex **2a**, its two different crystals **2b**, **2c** having two water, benzene solvent molecules as guest molecules carrying four bidentate β -diketonato ligands having eight aromatic moieties and one piperidinium as a counter cation. Further, we have investigated the structural properties using X-ray analyses.

The luminescent intensity of the complex was quite strong because all coordinate positions of central metal ion; europium was occupied by β -diketonato ligands. In other words, the complex has no water molecule as ligand, which in general utilizes the excited energy on the f orbital (5D levels) to the vibration relaxation of water molecule in solid and in solution state. Therefore, the excited energy on the f orbital (5D levels) of the centered europium ion is effectively relaxed to 7F levels only.

Our recent research reported that the octa-coordinate homoleptic and heteroleptic europate (III) complexes carrying four bidentate ligands were synthesized and the structure of the homoleptic complex was unexpectedly cone-like by X-ray analysis without water molecule(s) as the ligand(s) [13]. The luminescent intensity of the complex was quite strong because the complex has no water ligand in solid and in solution.

2. Experimental

2.1. Materials and Methods

Highly purity europium (III) chloride, piperidine was purchased from the TCI

chemicals industry, Tokyo and used as such without further purification. The ligand 1,3-diphenyl-1,3-propanedione was purchased from the Sigma Aldrich. The solvents and other reagents were purchased from the commercial source and used as such. The $^1\text{H-NMR}$ spectra were recorded on a Bruker AVANCE400S spectrometer (Bruker, Yokohama, Japan) in CDCl_3 with tetramethylsilane (Me_4Si) as an internal reference. The positive fast atom bombardment (FAB) mass spectrum (MS) of the complex were obtained on a Nippon Densi JEOL JMS-SX102A spectrometer (JEOL, Tokyo, Japan) using NBA (nitrobenzylalcohol) as the matrix and DCM (dichloromethane) as the solvent. The instrument was operated in positive ion mode over an m/z range of 100 - 2000. Elemental analysis data were recorded on a Yanako MT-4 analyzer (Yanako Group, Kyoto, Japan). A JASCO V-550 spectrophotometer (JASCO Corporation, Tokyo, Japan) was used for obtaining UV-Vis spectra in dichloromethane with 250 nm - 900 nm range. HITACHI F-2500 spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan) was used for fluorescence spectra measurements in dichloromethane with 250 nm - 900 nm range. CCDC No. 1561975, 1562869 and 1562868 contain the supplementary crystallographic data for the complexes **2a**, **2b** and **2c**, respectively.

2.2. Synthesis of Complex 2a and Its Two Different Crystals 2b, 2c by Crystallization Process

In a first Schlenk vessel, a solution of europium (III) chloride (0.650 g, 0.41 mmol) and 1,3-diphenyl-1,3-propanedione (0.370 g, 1.65 mmol) in absolute ethanol (30 mL) was prepared at room temperature. Under protection from air, slightly excess of piperidine (0.30 mL, 3.0 mmol) was added to the solution, and then, the two solutions were combined and stirred to at room temperature for 12 hours. After filtration, piperidine and most volatile materials were removed from the filtrate on a vacuum line. Under protection from air, the residue was repeatedly washed with small portions (5 mL) of warm, dry ethanol. The residual powders were dissolved with ethanol for crystallization. Without protection from air, the crystallized product was filtered off, washed with two portions of cold ethanol, and dried under reduced pressure, affording 0.371 g of pale-yellow piperidinium tetrakis (1,3-diphenyl-1,3-propanedionato) europate (III) **2a** as a powder in 80% yield. Crystallization of the complex was carried out using three different solvents (chloroform, ethanol, and benzene). Shapes of the obtained crystals were different; therefore, the three crystals may be including the solvent molecule(s).

M.p.: $>210^\circ\text{C}$ (decomp.).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ ppm 2.05 (br s, 2H, piperidinium), 3.30 (br s, 4H, piperidinium), 3.99 (br s, 4H, piperidinium), 4.98 (s, 4H, β -diketonato), 7.95 (br s, 2H, piperidinium N-H), 7.95 (m, 32H, phenyl), 8.05 (m, 8H, phenyl). Pos. FAB-MS: m/z 823 [(M + H) $^+$ -1 ligand-piperidinium cation], 1043, 1045 [(M + H) $^+$ -piperidinium cation]. Elemental analysis, Eu 13.50% (13.43%, calcd.), C 68.89% (69.02%, calcd.), H 4.94% (4.99%, calcd.), N 1.29% (1.24%, calcd.).

2.3. Single-Crystal X-Ray Analysis and Structure Determination

Crystals of two compounds **2a**, **2b** and **2c** were obtained at room temperature by crystallization in different solvents.

The crystal data were recorded on a Bruker APEX II KY CCD diffractometer equipped with graphite monochromatized (doubly curved silicon crystal) Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a sealed micro focus tube, and a nominal crystal to area detector distance of 58 mm. X-ray generator settings were 50 kV and 30 mA. The data were collected at -183°C (90 K). Data were acquired using four sets of Omega scans at different Phi settings and the frame width was 0.5° . Integration of the data yielded a total of 25,148 reflections to a maximum θ angle of 28.7° for the compound **2a**. And a total of 33,250 reflections to a maximum θ angle of 28.8° for the compound **2b**. And a total of 14,274 reflections to a maximum θ angle of 24.4° for the compound **2c**.

The crystallographic data of these complexes were summarized in **Table 1**. APEX2 software was used for preliminary determination of the unit cell [14].

Table 1. Crystallographic data for the complexes (**2a**, **2b** and **2c**).

	$\text{C}_{65}\text{H}_{56}\text{Eu}_1\text{N}_1\text{O}_8$	$\text{C}_{65}\text{H}_{59}\text{EuNO}_{10}$	$\text{C}_{71}\text{H}_{62}\text{Eu}_1\text{N}_1\text{O}_8$
Empirical formula	$\text{C}_{65}\text{H}_{56}\text{Eu}_1\text{N}_1\text{O}_8$	$\text{C}_{65}\text{H}_{59}\text{EuNO}_{10}$	$\text{C}_{71}\text{H}_{62}\text{Eu}_1\text{N}_1\text{O}_8$
Formula weight	1162.06	1166.09	1209.18
Temperature	90 K	90 K	90 K
Wavelength	0.71073 \AA	0.71073 \AA	0.71073 \AA
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	Cc (no. 9).	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
Unit cell dimensions	a = 23.5955 (18) \AA b = 23.5312 (18) \AA c = 19.1829 (15) \AA $\beta = 91.4500$ (10°)	a = 16.128 (4) \AA b = 18.411 (5) \AA c = 18.912 (5) \AA $\beta = 92.992$ (3°)	a = 11.0948 (5) \AA b = 19.7927 (9) \AA c = 26.8063 (12) \AA $\beta = 99.06$ (3°)
Cell volume	10647.5 (14) \AA^3	5608 (3) \AA^3	5813.1 (5) \AA^3
Z	8	4	4
Density (calculated)	1.450 g/cm^3	1.376 g/cm^3	1.382 g/cm^3
Absorption coefficient	1.242 mm^{-1}	1.179 mm^{-1}	1.138 mm^{-1}
F (000)			
Crystal size (mm)	4760	2396	2488
Theta range for data collection	$0.300 \times 0.300 \times 0.250$	$0.300 \times 0.300 \times 0.250$	$0.300 \times 0.300 \times 0.250$
Index ranges	1.22° to 25.24°	1.54° to 20.48°	1.28° to 28.78°
Reflections collected			
Independent reflections	$-30 \leq h \leq 30$, $-31 \leq k \leq 31$, $-24 \leq l \leq 24$	$-14 \leq h \leq 15$, $-26 \leq k \leq 26$, $-35 \leq l \leq 35$	$-14 \leq h \leq 15$, $-26 \leq k \leq 26$, $-35 \leq l \leq 35$
Reflections [$I > 2\sigma(I)$]			
Completeness to theta $^\circ$	62,052	5574	68,014
Absorption correction	25148 [R(int) = 0.0276]	33250 [R(int) = 0.095]	14274 [R(int) = 0.0321]
Refinement method			
	99.9%	99.7%	94.3%
Data/restraints/parameters	Empirical	Empirical	Empirical
Goodness-of-fit on F^2	Full-matrix LS on F^2	Full-matrix LS on F^2	Full-matrix LS on F^2
Final R_1 indices [$I > 2\sigma(I)$]	5575/2/1351	5574/0/695	14274/0/730
wR_2 indices (all data)	1.094	1.251	1.100
Largest diff. peak and hole	$R_1 = 0.0344$ $wR_2 = 0.0986$ 1.307 and -1.022 e\AA^{-3}	$R_1 = 0.0717$ $wR_2 = 0.2106$ 2.51 and -1.62 e\AA^{-3}	$R_1 = 0.0258$ $wR_2 = 0.0798$ 0.703 and -0.784 e\AA^{-3}

Determination of integrated intensities and unit cell refinement were performed using SAINT program [15]. The structures were solved with SHELIXS-2014/7 [16] and subsequent structure refinements were performed with SHELIX-L2014/7.

3. Results and Discussion

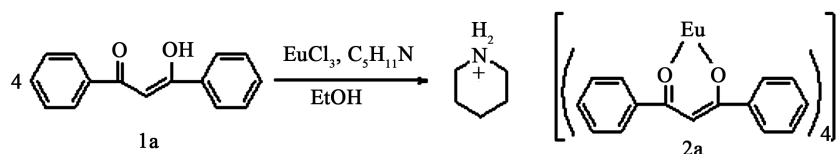
Synthetically, piperidinium [tetrakis(1,3-diphenyl-1,3-propanedionato)europate (III)] complex **2a** is obtained in 80% isolated yield from the corresponding ligand 1,3-diphenyl-1,3-propanedione by complexation reaction with europium (III) chloride in the presence of piperidine (**Scheme 1**). This reaction is a standard preparation procedure for lanthanide (III) complex [17]. Structural properties in solution are in line with expectations, as shown by ¹H NMR spectroscopy. Although the peaks of the complex are quite shifted from normal regions due to paramagnetic effect of the europium (III) ion, it can be easily assigned.

In the pos. MS spectrum, the fragment peak is m/z 823 [(M + H)⁺-1 ligand-piperidinium cation] mainly appears. On the contrary, the peak m/z 1043, 1045 [(M + H)⁺-piperidinium cation] are quite small. The reason is well explained that the neutral fragment is more stable than that of anionic fragment ion.

We have measured UV-Vis and Fluorescence spectra of complex **2a** as well as its other two crystals **2b** and **2c**. The results were quite similar. In other words, the presence of two water and one benzene solvent molecules in the crystals of **2b** and **2c** did not affect the UV-Vis and Fluorescence properties of complex **2a**. Due to this reason, here we discussed UV-Vis and Fluorescence properties of complex **2a** only.

The UV-vis absorptions for the europium complex **2a** was measured in dichloromethane solution (1×10^{-5} mol/L), and the corresponding spectra is shown in **Figure 1**. The complex **2a** showed strong absorption band 352 nm. These strong absorption bands were assigned to the π - π^* enol absorptions of the β -diketone ligand. Relatively low intensity absorption bands at 225 nm and 270 nm were assigned to the n - π^* enol absorptions of the β -diketone ligands. The molar extinction coefficient of the complex **2a** was 9×10^4 (352 nm) L·mol⁻¹·cm⁻¹. This was attributed to the effective chelating of four β -diketone ligands with the europium (III) ion.

The emission spectra of the europium complex **2a** was measured in dichloromethane solution (1×10^{-5} mol/L), and the corresponding spectra is shown in **Figure 2**. Emission spectra of the complex **2a** was measured by exciting the complex at their absorption maxima wavelength 352 nm. The emission spectra of the complex **2a** showed sharp peaks in the region 590 - 720 nm associated



Scheme 1. Preparation of piperidinium tetrakis(1,3-diphenyl-1,3-propanedionato) europate (III).

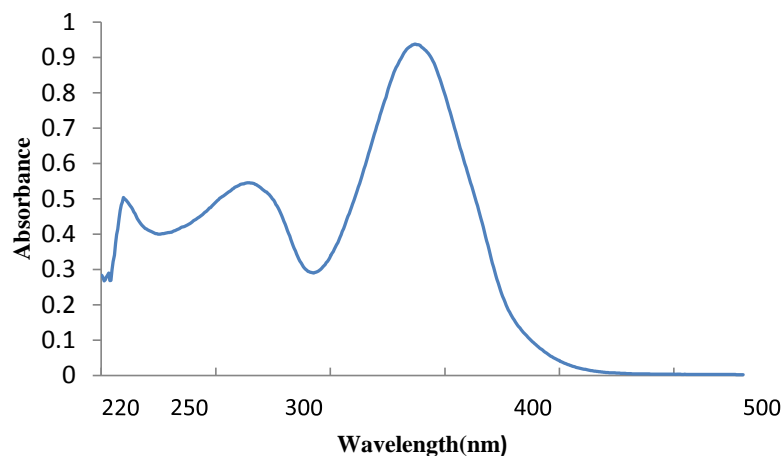


Figure 1. UV-Vis spectra of complex **2a**.

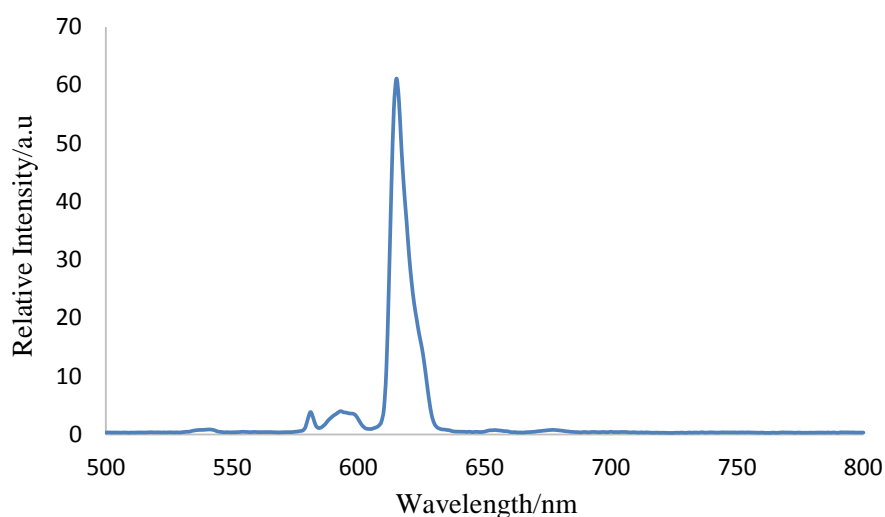


Figure 2. Emission spectra of the complex **2a**.

with ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0 - 4$) transitions of the europium (III) ion. The very high intensity peak was observed at 613 nm due to the ${}^5D_0 \rightarrow {}^7F_2$ transition, suggesting a highly polarizable chemical environment around the europium (III) ion [18]. This transition was responsible for the red emission of the complex **2a**.

Suitable single crystals for X-ray structure analysis were easily obtained for the complex **2a**. In principle, europium (III) complexes are not sensitive against air, therefore, preparation and purification of the complex is quite easy. Crystallization of the complex **2a** was carried out using three different solvents (chloroform, ethanol, and benzene) that resulted in crystals of complex **2a** and its other two crystals **2b**, **2c** having solvent molecules in their cavity.

Molecular shapes of these complexes are fused dual-cone like structures and the complex molecules have cavities (Figure 3). The complex **2a** crystallizes in the monoclinic space groups Cc (centrosymmetric, No.13), the cell unit includes four molecules with four piperidinium ions and with no solvate molecule (Figure 3).

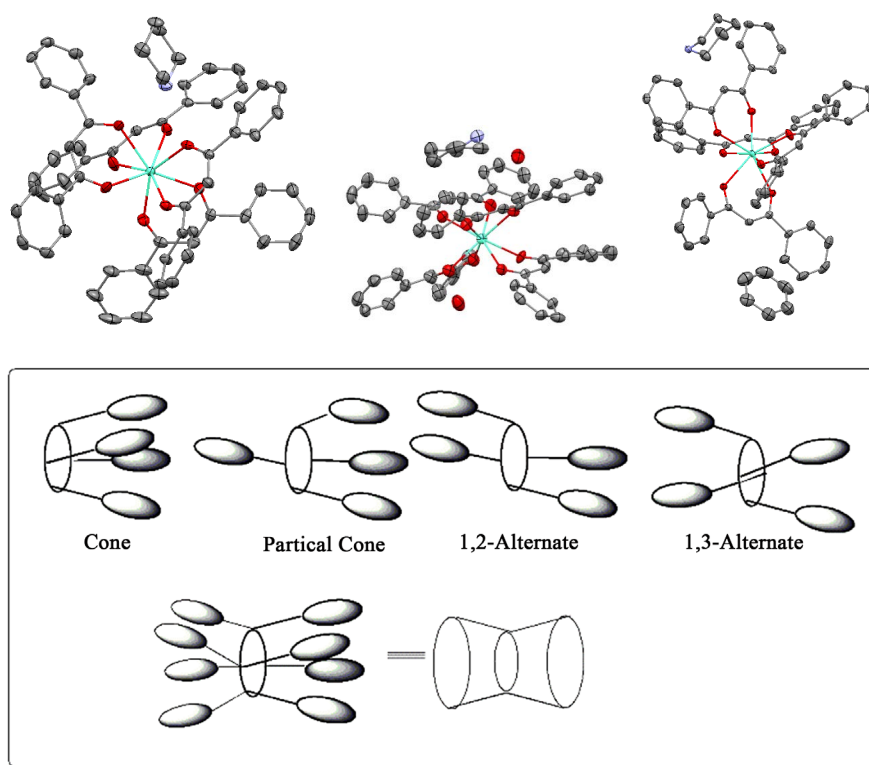


Figure 3. ORTEP view of the complexes **2a** (left), **2b** (center) and **2c** (right). Ellipsoids are drawn at 50% probability level. Aqua blue, blue and red ellipsoids show Eu, N and O atom(s), respectively.

The complex **2b** crystallizes in the monoclinic space groups $P2_1/n$ (centrosymmetric, No.14); the cell unit includes four molecules with four piperidinium ions and with eight water molecules (**Figure 3**). The complex **2c** also crystallizes in the monoclinic space group $P2_1/n$ (centrosymmetric, No.14), the cell unit includes four molecules with four piperidinium ions and with four benzene molecule (**Figure 3**). The three crystals have quite complex molecular packing arrangement (**Figure 4**).

The europium (III) ions of **2a**, **2b** and **2c** are coordinated by a distorted octahedral arrangement of eight oxygen atoms from four chelating β -diketonato ligands. The average Eu1-O (1 - 8) bond lengths are moderately normal, and these values are ca.2.378 Å for **2a**, 2.389 Å for **2b** and 2.391 Å for **2c**, respectively. The bond angles in the five membered rings consisting of Eu and 1,3-butanedionato ligands (O-Eu-O) vary from 69.7 (2)° to 71.7 (1)° for **2a**, 68.9 (3)° to 71.3 (3)° for **2b** and 70.45 (5)° to 71.01 (5)° for **2c**, respectively (**Tables 2-4**). These values of bond distances and bond angles are in good agreement with those reported for other analogous Eu- β -diketonato complexes [19]. The piperidinium cation involving the N1 atom is most stable chair form in the crystal.

Molecular shapes of these complexes are fused double-cone like structures and the complex molecules have cavities (**Figure 3**). The difference between **2a**, **2b** and **2c** about the inclusion of solvate molecule is well explained that the difference of the largeness of the cavity consisting of the four ligands. The cavity

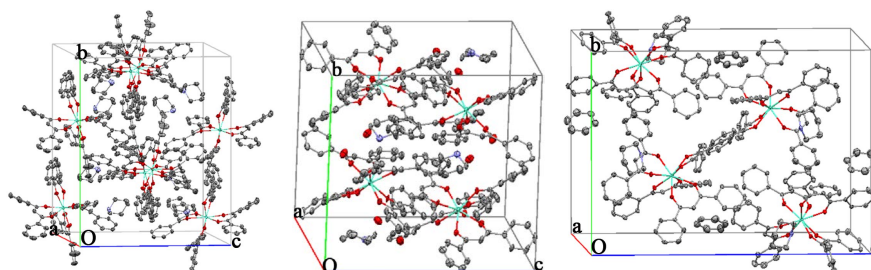


Figure 4. Crystal packing diagram of the complexes **2a** (above) and **2b** (below). Aqua blue, pale green, darkblue, red and green ellipsoids show Eu, F, N, O and Cl atoms, respectively.

Table 2. Selected bond lengths (Å) and angles (°) for the complex **2a**.

Eu1-O1	2.354 (5)	Eu1-O2	2.361 (4)
Eu1-O3	2.485 (6)	Eu1-O4	2.350 (5)
Eu1-O5	2.339 (4)	Eu1-O6	2.385 (4)
Eu1-O7	2.363 (4)	Eu1-O8	2.394 (4)
O1-Eu1-O2	71.1 (2)	O3-Eu1-O4	69.7 (2)
O5-Eu1-O6	71.1 (2)	O7-Eu1-O8	71.7 (1)

Table 3. Selected bond lengths (Å) and angles (°) for the complex **2b**.

Eu1-O1	2.359 (8)	Eu1-O2	2.353 (8)
Eu1-O3	2.371 (7)	Eu1-O4	2.388 (4)
Eu1-O5	2.471 (8)	Eu1-O6	2.388 (8)
Eu1-O7	2.397 (8)	Eu1-O8	2.392 (8)
O1-Eu1-O2	71.3 (3)	O3-Eu1-O4	70.4 (3)
O5-Eu1-O6	68.9 (3)	O7-Eu1-O8	70.8 (3)

Table 4. Selected bond lengths (Å) and angles (°) for the complex **2c**.

Eu1-O1	2.343 (3)	Eu1-O2	2.374 (2)
Eu1-O3	2.347 (1)	Eu1-O4	2.458 (1)
Eu1-O5	2.407 (1)	Eu1-O6	2.382 (1)
Eu1-O7	2.408 (2)	Eu1-O8	2.413 (1)
O1-Eu1-O2	70.45 (5)	O3-Eu1-O4	71.01 (5)
O5-Eu1-O6	70.78 (5)	O7-Eu1-O8	70.49 (5)

sizes of the complex **2a** seems to be larger. The large cavity sizes of the complex **2a** facilitated the inclusion of water and benzene solvate molecules. Differences between these complexes and Calix [4] arene are environments internal spaces of cavities, in another words, aromatic parts on the Calixarenes are oriented π -electron surfaces to the cavity center. On the contrary, the aromatic parts on the complexes are oriented aromatic C-H protons to the cavity center. Therefore, the complex **2a**, expected as new compound for undeveloped field of host-guest chemistry.

4. Conclusion

In conclusion, we reported the synthesis, characterization, crystal structure and photophysical properties of piperidinium [tetrakis(1,3-diphenyl-1,3-propanedionato) europate (III)] complex **2a**. Its two different crystals **2b**, **2c** having water, benzene solvent molecules were readily prepared by crystallization process. Complex **2a** was characterized by ¹H-NMR spectroscopies, positive FAB-Mass, and Elemental Analysis. Further their exact molecular structures of **2a**, **2b** and **2c** were determined by X-ray analysis. The UV-Vis, Fluorescence properties of all three crystals remained same in solid as well as in solution state. Complex **2a** exhibited strong red emission at 613 nm, which could find prominent applications in light emitting devices. These strong emissions were attributed to the ⁵D₀ → ⁷F₂ transition of Europium (III) ions under UV excitation.

Acknowledgements

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