Crystal Structure Theory and Applications, 2021, 10, 1-13
https://www.scirp.org/journal/csta
ISSN Online: 2169-2505
ISSN Print: 2169-2491

Design, Synthesis, Crystal Structure and Photoluminescence Properties of Four New Europium (III) Complexes with Fluorinated β-Diketone Ligand

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How to cite this paper: Moriguchi, T., Kawata, H. and Jalli, V. (2021) Design, Synthesis, Crystal Structure and Photoluminescence Properties of Four New Europium (III) Complexes with Fluorinated β-Diketone Ligand. *Crystal Structure Theory and Applications*, **10**, 1-13.
https://doi.org/10.4236/csta.2021.101001

Received: January 12, 2021
Accepted: February 1, 2021
Published: February 4, 2021

Abstract

The strong photoluminescence properties of europium complexes with organic ligands attracted the attention of many researchers and found a wide range of uses in medical, industrial and biological fields. In this article, four new Tetrakis europium complexes **3a**, **3b**, **3c** and **3d** have been prepared using 1-phenyl-4,4,4-trifluoro-1,3-butenedionato ligand and pyridinium, bipyridinium, piperazinium and piperidinium counter cations. These complexes have been characterized by negative FAB-mass. The crystal structures of **3a**, **3b**, **3c** and **3d** were determined by single crystal X-ray diffraction analysis. The complex **3a** crystallized in monoclinic form, space group $P2_1/n$ with four molecules in the unit cell. The complex **3b** crystallized in monoclinic form, space group $P2/n$ with two complex molecules in the unit cell. The complex **3c** crystallized in monoclinic form, space group $C2/c$ with sixteen molecules in the unit cell. The complex **3d** crystallized in monoclinic form, space group $P2_1/n$ with four complex molecules in the unit cell. The complex **3a** has 1,2-alternative structure, **3b** has 1,3-alternative structure, **3c** has cone like structure and **3d** has partial cone like structure. The photoluminescence properties of these complexes have been evaluated. Strong red emissions were observed in all four complexes due to $^5D_0 \rightarrow {}^7F_2$ transition of Europium (III) ions under UV excitation. Four β-diketone ligands acted as strong antenna ligands and transferred the absorbed energy to europium (III) ion effectively; consequently strong red luminescence was observed.

Keywords

Tetrakis Europium Complexes, Luminescence, Fluorinate β-Diketone Ligand,

Pyridine, Bipyridine, Piperazine, Bipiperidine

1. Introduction

The photoluminescence properties of Lanthanide complexes with organic ligands have been greatly enhanced, and led to the development of strong luminescent Lanthanide complexes with important applications in medical, industrial and biological fields [1]-[7]. Europium (III) complex with organic ligands is an example of strong luminescent Lanthanide complex and Europium (III) complexes that have great importance in materials engineering chemistry due to significant improvement in photophysical parameters such as high luminescence emission efficiency, long fluorescence life time, large stokes shift, sharp emission bands [8] [9] [10] [11]. In the past decade various high luminescent europium complexes have been engineered and evaluated for their photoelectronic properties such as OLEDs, electroluminescent displays, bioimaging, sensing and targeting specific DNA structures, melamine detection in milk protein. Europium (III) complexes have also found applications as sensor materials to detect pesticides, temperature, HCl, NO_2 gas, HOCl, pH, phosphate, mitochondria and, 8-oxo-dGTP [12]-[20]. Albumin proteins in human serum have also been detected by Europium complexes, which act as sensor materials [21].

Search for novel europium complexes that uses less energy and exhibits desired application such as sensors, OLEDS, etc. is of great importance in photoelectronic materials. Therefore, new europium complexes should have enhanced degree of change in luminescence to be a good sensor material. On the other hand, understanding the relationship between molecular structures and photoelectronic properties of europium (III) complexes gives valuable information in designing future photoelectronic materials with improved properties. It is stated that luminescence of Europium (III) ion originates from forbidden f-f transitions that totally hinder the Europium (III) ion interaction with light. The ligand that forms complexes with Europium (III) ion acts as antenna. This absorbs energy and transfers to Europium (III) ion through intersystem crossing to triplet excited states. In this context, europium complexes with substituted aromatic β-diketones as organic ligands were explored due to efficiency in generating triplet excited states in close contact with europium (III) ion. Thus, various Europium (III) complexes with β-diketones were synthesized and evaluated for their photoluminescent properties [22] [23] [24] [25] [26].

In our previous studies, we synthesized and investigated the molecular structures and photoelectronic properties of octa-coordinate europate (III) complexes using substituted β-diketone ligands [27] [28]. In this study, we want to investigate the molecular structures and photoluminescence properties of four new octa-coordinate Europium (III) complexes **3a**, **3b, 3c** and **3d**, possessing pyridinium, bipyridinium, piperazinium and bipiperidinium as counter cations.

2. Experimental

2.1. Materials and Methods

Reagent grade europium (III) chloride, pyridine, bipyridine, piperazine and bipiperidine were purchased from the TCI chemicals industry, Tokyo and used as such to prepare europium complexes. The ligand 1-phenyl-4,4,4-trifluoromethyl-1,3-butanedione was synthesized in the laboratory. The positive fast atom bombardment (FAB) mass spectrum (MS) of the complexes was obtained on a Nippon Densi JEOL JMS-SX102A spectrometer (JEOL, Tokyo, Japan) using NBA (nitrobenzyl alcohol) as the matrix and DCM (dichloromethane) as the solvent. The instrument was operated in negative 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 - 900 nm range. HITACHI F-8700 spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan) was used for fluorescence spectra measurements in dichloromethane with 250 - 900 nm range. CCDC No. 1962454, 2047729, 1563207 and 1563206 contain the supplementary crystallographic data for the complexes **3a**, **3b, 3c** and **3d**, respectively.

2.2. General Procedure for the Synthesis of Complexes 3a, 3b, 3c and 3d

In a RB flask, a solution of europium (III) chloride (0.650 g, 0.41 mmol) and 1-phenyl-4,4,4-trifluoromethyl-1,3-butanedione **1** (0.370 g, 1.65 mmol) in absolute ethanol (30 mL) was prepared at room temperature. Under protection from air, slightly excess of pyridine, bipyridine, piperazine, bipiperidine were added to the solution to get complexes **3a**, **3b**, **3c** and **3d** respectively. Ethanol was removed by rotary evaporator under reduced pressure. Under protection from air, the residue was repeatedly washed with small portions (5 mL) of warm, dry ethanol. The residual powders were dissolved in 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 the complexes **3a**, **3b**, **3c** and **3d** as a powder. All four complexes were obtained in moderate to good yields (68% for **3a**, 65% for **3b**, 75% for **3c** and 60% for **3d**, respectively).

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

Crystals of four compounds **3a**, **3b, 3c** and **3d** were obtained at room temperature by crystallization in DCM-ethanol mixed solvent.

The crystal data were recorded on a Bruker APEX II KY CCD diffractometer equipped with graphite monochromatized Mo-Kα radiation of wavelength 0.71073 Å 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 −153˚C (120 K) for **3b**-**3c** and at −123˚C (150 K) for **3a**.

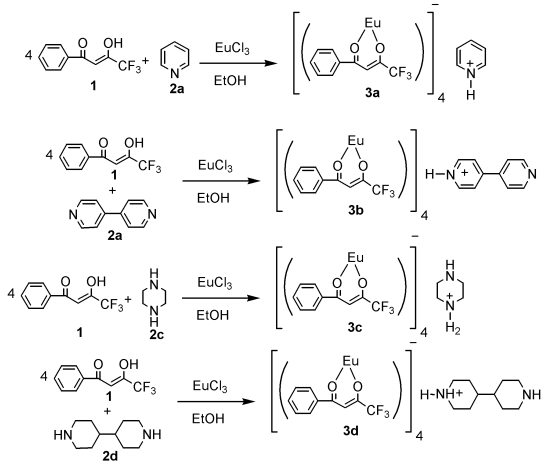
The crystallographic data of these complexes were summarized in Table 1. APEX2 software was used for preliminary determination of the unit cell [29]. Determination of integrated intensities and unit cell refinement were performed using SAINT program [30]. The structures were solved with SHELXS-2014/7 [31] and subsequent structure refinements were performed with SHELXL-2014/7.

3. Results and Discussion

Complexes **3a**, **3b**, **3c** and **3d** were synthesized from the corresponding ligand 1,3-diphenyl-1,3-propanedione by complexation reaction with europium (III) chloride in the presence of pyridine, bipyridine, piperazine and bipiperidine as counter cations (Scheme 1). This reaction is a standard preparation procedure

Table 1. Crystallographic data for the complexes (**3a, 3b, 3c** and **3d**).

Parameters measured	**3a**	**3b**	**3c**	**3d**
Empirical formula	$C_{45}H_{30}Eu_1F_{12}NO_8$	$C_{50}H_{33}Eu\ F_{12}N_2O_8$	$C_{44}H_{35}Eu_1\ F_{12}N_2O_8$	$C_{45}H_{35}Eu_1F_{12}NO_8$
Formula weight	1092.67	1169.8	1099.71	1097.71
Crystal shape, color	Prism, colorless	Prism, colorless	Prism, colorless	Prism, colorless
Temperature	150 K	120 K	120 K	120 K
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2/n$	$C2/c$	$P2_1/n$
Unit cell dimensions	a = 11.144 (11) Å b = 22.034 (2) Å c = 18.770 (2) Å β = 107.112 (1)˚	a = 12.711 (4) Å b = 12.672 (4) Å c = 14.755 (5) Å β = 99.126 (3)˚	a = 36.894 (5) Å b = 22.068 (3) Å c = 21.916 (3) Å β = 92.682 (1)˚	a = 11.547 (19) Å b = 21.886 (4) Å c = 18.005 (3) Å β = 99.550 (2)˚
Cell volume	4405.1 (8) Å^3	2360.9 (13) Å^3	17,825 (1) Å^3	4487.1 (13) Å^3
Z	4	2	16	4
Calculated density	1.648 g/cm^3	1.643 g/cm^3	1.639 g/cm^3	1.625 g/cm^3
Absorption coefficient	1.53 mm^{-1}	1.433 mm^{-1}	1.512 mm^{-1}	1.501 mm^{-1}
F (000)	2168	1164	8768	2188
Crystal size (mm)	0.35 × 0.35 × 0.10	0.20 × 0.15 × 0.10	0.43 × 0.25 × 0.10	0.15 × 0.15 × 0.10
T Theta range for data collection	1.5˚ to 29˚	1.54˚ to 20.48˚	1.075˚ to 25.027˚	1.48˚ to 24.97˚
Limiting Indices	$-14 \le h \le 14$, $-29 \le k \le 29$, $-24 \le l \le 24$	$-15 \le h \le 15$, $-15 \le k \le 15$, $-17 \le l \le 17$	$-43 \le h \le 43$, $-26 \le k \le 26$, $-26 \le l \le 26$	$-13 \le h \le 13$, $-25 \le k \le 25$, $-21 \le l \le 21$
Reflections	52,471/11,725	4258/20,234	15,738/84,697	7862/41,761
collected/unique	[R(int) = 0.037]	[R(int) = 0.084]	[R(int) = 0.0321]	[R(int) = 0.049]
Completeness to theta ˚	100%	99.0%	99.9%	99.8%



Scheme 1. Reaction scheme for the preparation of **3a**, **3b**, **3c** and **3d**.

for lanthanide (III) complex [32]. Structures of complexes were determined by mass spectrometry and X-ray single crystal structure analyses.

We have measured the UV-Vis and Fluorescence spectra of **3a**, **3b**, **3c** and **3d**. The UV-Vis and Fluorescence spectra of **3a**, **3b**, **3c** and **3d** were measured in solution phase (dichloromethane, 1×10^{-5} mol/L).

The fluorescence spectrum was measured in solution and solid state as well. The solution state fluorescence measurements were carried out in dichloromethane solution (1×10^{-3} mol/L). The corresponding absorption and emission spectrum of **3a**, **3b**, **3c** and **3d** were shown below (**Figures 1-8**, respectively). Complexes **3a**, **3b**, **3c** and **3d** exhibited absorption maxima at 327, 330, 326 and 313 nm, respectively. These strong absorption bands were assigned to the π-π* enol absorptions of the *β*-diketone ligand.

The fluorescence spectrum of **3a** was measured by exiting the complex at 379 nm in solution and 307 nm in solid state. Strong emission band was observed from 600 to 630 nm. The complex **3b** was exited at 379 nm in solution and 368 nm in solid state. Strong emission band was observed from 590 to 620 nm.

The fluorescence spectrum of **3c** was measured by exiting the complex at 378 nm in solution and 307 nm in solid state. Strong emission band was observed from 600 to 650 nm. The complex **3d** was exited at 377 nm in solution and 306 nm in solid state. Strong emission band was observed from 610 to 653 nm.

Suitable single crystals for X-ray structure analysis were easily obtained for all complexes. Since, europium (III) complexes are air stable, preparation of crystals is has been easy. All four complexes were dissolved in suitable solvents and left to slow evaporation at room temperature that resulted in crystals of complex **3a**, **3b**, **3c** and **3d**.

The complex **3a** has 1,2-alternative structure, **3b** has 1,3-alternative structure, **3c** has cone like structure and **3d** has partial cone like structure. In the crystal, complex **3a** crystallized in monoclinic form with $P2_1/n$ space group and it has four molecules in unit cell with pyridinium cation (**Figure 9**). The complex **3b** also crystallize monoclinic form with $P2/n$ space group and it has two molecules

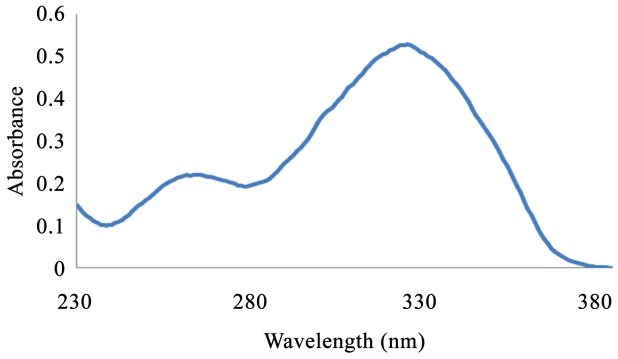


Figure 1. UV-Vis spectra of complex **3a**.

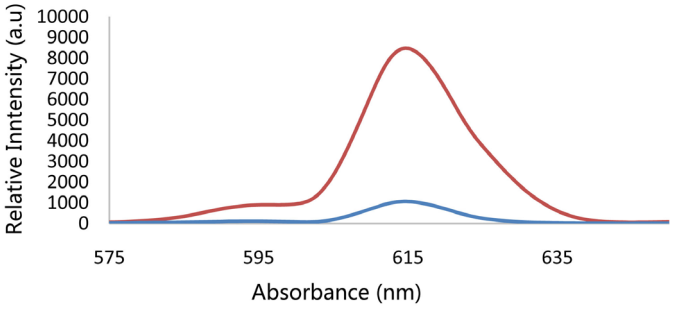


Figure 2. Emission spectra of complex **3a**. Blue and red color represents, spectrum in solution and solid phase, respectively.

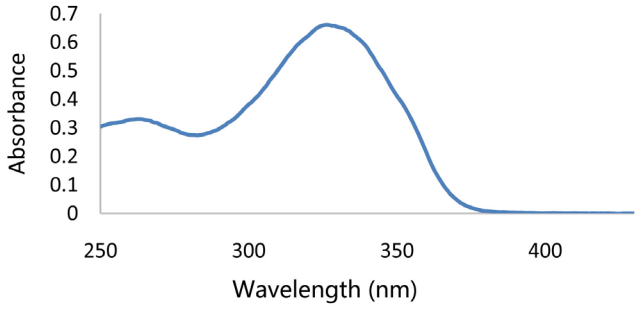


Figure 3. UV-Vis spectra of complex **3b**.

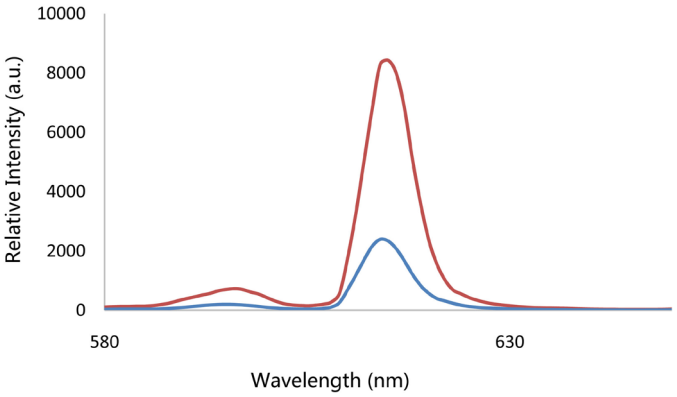


Figure 4. Emission spectra of complex **3b**. Blue and red color represents, spectrum in solution and solid state, respectively.

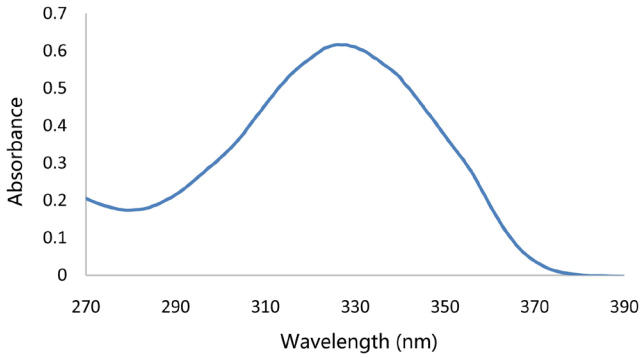


Figure 5. UV-Vis spectra of complex **3c**.

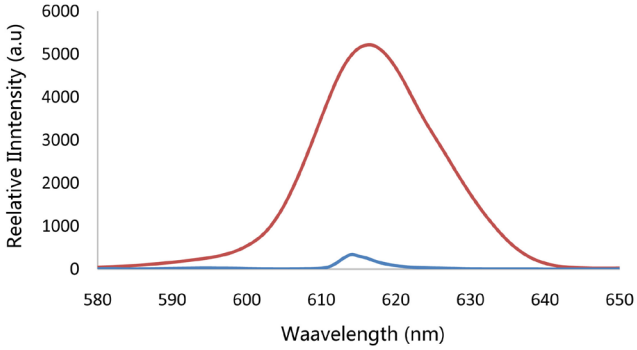


Figure 6. Emission spectra of complex **3c**. Blue and red color represents, spectrum in solution and solid state, respectively.

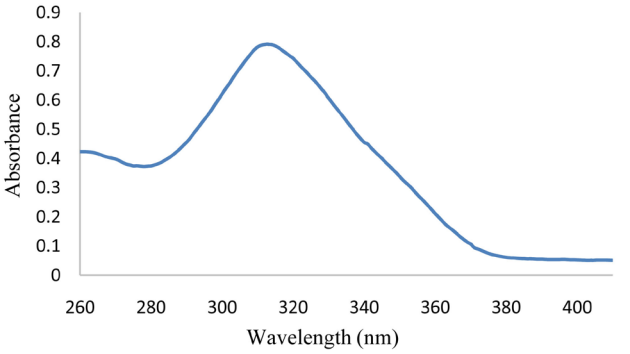


Figure 7. UV-Vis spectra of complex **3d**.

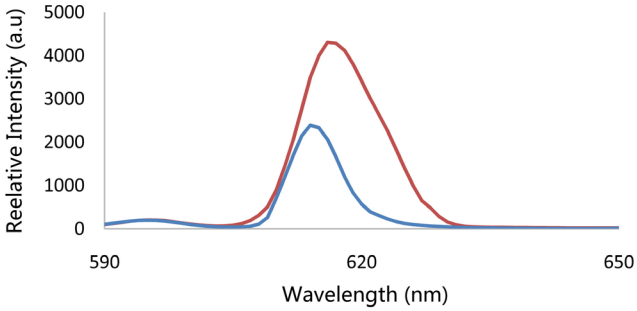


Figure 8. Emission spectra of complex **3d.** Blue and red color represents, spectrum in solution and solid state, respectively.

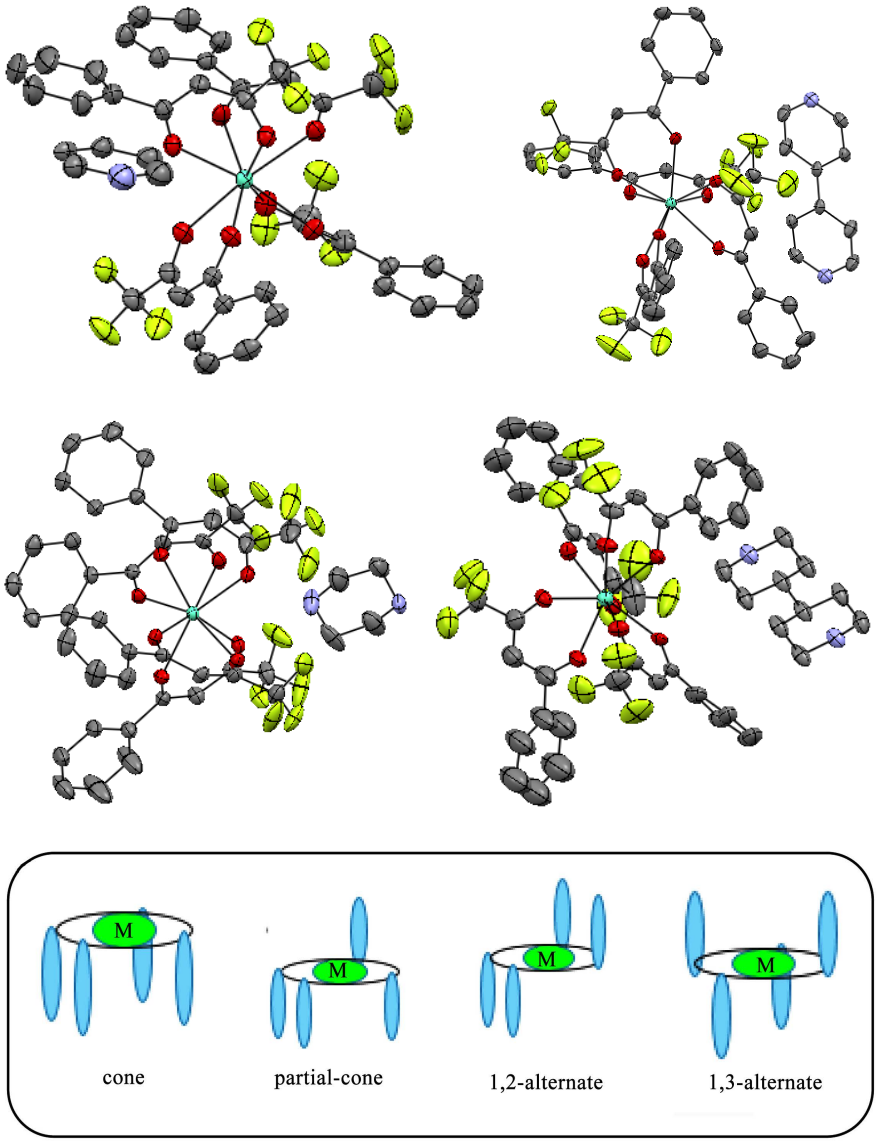


Figure 9. ORTEP view of the complexes **3a**, **3b**, **3c** and **3d**. Ellipsoids are drawn at 50% probability level. Aqua blue, blue and red ellipsoids show Eu, N and O atom(s), respectively.

in unit cell with bipyridinium monocation. The complex **3c** crystallized in monoclinic form with $C_{2/C}$ space group and it has sixteen molecules in unit cell with piperazinium cation. The complex **3d** also crystallized in monoclinic form with $P2_1/n$ space group and it has two molecules in unit cell with bipiperidinium cation.

The europium (III) ions of four complexes are coordinated by a distorted octahedral arrangement of eight oxygen atoms from four chelating β-diketone ligands (**Figure 10**). The average Eu1-O bond lengths are moderately normal, and these values are 2.384Å for **3a**, 2.40 Å for **3b**, 2.39Å for **3c** and 2.38Å for **3d**, respectively (**Tables 2-5**). The bond distances and bond angles are in good agreement with those reported for other analogous Eu-β-diketone complexes [33].

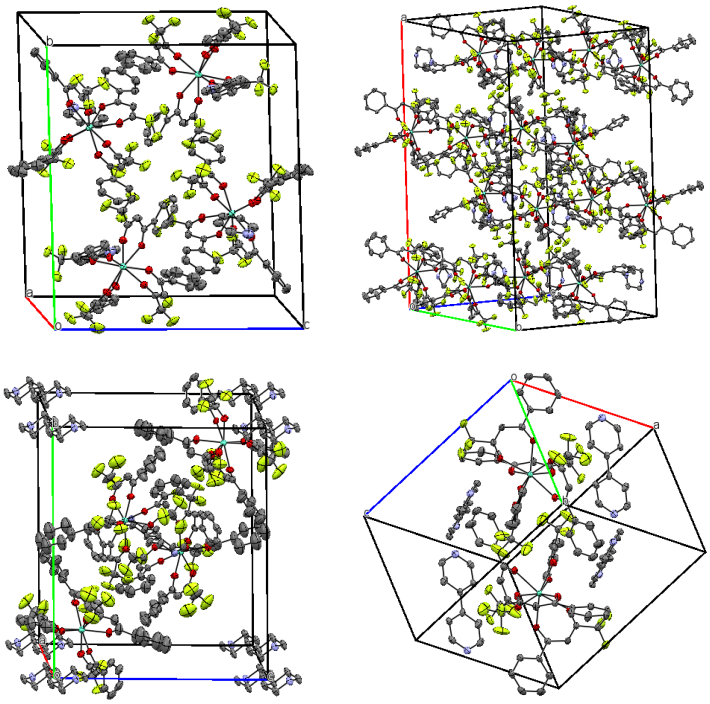


Figure 10. Crystal packing diagram of the complexes 3**a, 3b, 3c** and **3d** respectively. Aqua blue, pale green, darkblue, red and green ellipsoids show Eu, F, N, O and Cl atoms, respectively.

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

Eu1-O1	2.365 (2)	Eu1-O2	2.390 (2)
Eu1-O3	2.399 (2)	Eu1-O4	2.370 (2)
Eu1-O7	2.390 (2)	Eu1-O8	2.394 (4)
O1-Eu1-O2	91.6 (7)	O3-Eu1-O4	81.92 (6)
O7-Eu1-O8	149.53 (7)		

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

Eu1-O1	2.392	Eu1-O2	2.394
Eu1-O3	2.408	Eu1-O4	2.409
O1-Eu1-O2	71.7	O3-Eu1-O4	73.3
O1-Eu1-O4	96.2	O2-Eu1-O3	129

Table 4. Selected bond lengths (Å) and angles (˚) for the complex **3c**.

Eu1-O1	2.387 (3)	Eu1-O2	2.412 (2)
Eu1-O3	2.403 (3)	Eu1-O4	2.370 (3)
Eu1-O5	2.373 (2)	Eu1-O6	2.354 (3)
Eu1-O7	2.429 (2)	O3-Eu1-O4	157.02 (9)
O1-Eu1-O2	70.14 (9)	O5-Eu1-O7	69.24 (9)
O5-Eu1-O6	117.99 (9)		

Table 5. Selected bond lengths (Å) and angles (˚) for the complex **3d**.

Eu1-O1	2.375 (7)	Eu1-O2	2.346 (7)
Eu1-O3	2.401 (6)	Eu1-O4	2.382 (5)
Eu1-O5	2.424 (7)	Eu1-O6	2.382 (6)
Eu1-O7	2.377 (6)	Eu1-O8	2.355 (7)
O1-Eu1-O2	70.9 (2)	O3-Eu1-O4	70.2 (2)
O5-Eu1-O6	71.0 (2)	O7-Eu1-O8	72.5 (2)

4. Conclusion

In conclusion, four new europium complexes have been synthesized and characterized. Further, molecular structures and photoelectronic properties of four europium complexes were determined. All four complexes exhibited strong emission between 590 - 640 nm, which could find prominent applications in light emitting devices. The absorbance and emission of the four complexes are quite the same. The fluorescence properties of all four crystals were very strong in solid state and very weak in solution state. These strong emissions were attributed to the $^5D_0 \rightarrow {}^7F_{0\text{-}4}$ transition of Europium (III) ions under UV excitation. To further improve the scope of applications of these complexes, introduction of electron withdrawing groups such as -CN, -F on phenyl rings of fluorinated β-diketone ligand may improve the photoluminescence intensity and emission life time.

Acknowledgements

We are grateful to the Center for Instrumental Analysis, Kyushu Institute of Technology (KITCIA) for negative FAB-mass, and X-ray analysis.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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