Original Article

Bulletin of Pure and Applied Sciences.
Vol.37 C (Chemistry), No.1, 2018: P.64-69
Print version ISSN 0970 4620
Online version ISSN 2320 320X
DOI 10.5958/2320-320X.2018.00009.2

Sensitized luminescence from novel pyrazolone based β-diketonate complexes of Eu^{3+}

D.B. Ambili Raj[1]*, S.V. Manoj[1], and B.S. Vinod[1]

Author Affiliations
[1]P.G. & Research Department of Chemistry, SreeNarayana College, Kollam 691001

Corresponding Author
***D.B. Ambili Raj,** P.G. & Research Department of Chemistry, SreeNarayana College, Kollam 691001

E-mail: ambilrajdb@gmail.com

Received on 13th January 2018
Accepted on 26th January 2018

Abstract

New pyrazolone based fluorinated ligand**,** 3–methyl 4–(2,2,3,3,3–penta fluoro–1–hydroxypropylidene)–1–phenyl–1H–pyrazol–5(4H)–one has been synthesized and well characterized. Europium–containing complexes were synthesized by adduct formation between 3–methyl 4–(2, 2, 3, 3, 3-penta fluoro–1–hydroxypropylidene)–1–phenyl–1H–pyrazol–5(4H)–one and europium (III) complex and a bidentate neutral donor 1,10–phenanthroline (phen). The emission spectra of the complexes display characteristic sharp peaks in the 575–700 nm region associated with the $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions of the Eu^{3+} ion.

Keywords: Lanthanide complex, PL properties, pyrazolone, fluorinated ligand, Eu^{3+}

1. INTRODUCTION

Lanthanide ions possess fascinating optical properties and are largely involved in various technological applications which are largely governed by their interaction with light. Light emitting diodes (LED's), television and computer displays, optical fibres, optical amplifiers, lasers, as well as responsive luminescent stains for biomedical analysis, medical diagnosis, and cell imaging rely heavily on lanthanide ions [1]. The two most useful lanthanides, Eu^{3+} and Tb^{3+}, have unusual spectroscopic characteristics, including longer lifetime (milliseconds), very sharp emission bands, and large Stokes shifts [2]. Unfortunately, as a consequence of the parity (Laporte) forbidden nature of the 4*f* transitions, the direct absorption of Ln(III) cations is only very weak, and they hence have very low molar absorption coefficients (typically less than 10 $M^{-1}cm^{-1}$) and hence a lower emission which limits their practical usage. In order to circumvent these lower values of extinction coefficients, the luminescent metal ion can be chelated to a chromophore–containing group which functions as an 'antenna,' by absorbing incident light and transferring this excitation to the metal ion, which can then deactivate by undergoing its typical luminescent emission. This process of 'antenna effect' will only be effective if the triplet level of the ligand is situated slightly above the accepting energy levels of the lanthanide ion. This is because the accepting energy levels of the visible luminescent lanthanides are all situated at relatively high energy position of UV region in the spectra. Among these antenna molecules, β–diketone ligand is one kind of important antennae for the Eu^{3+} and Tb^{3+} ions [3]. β–diketonates, as they are negatively charged bidentate ligands can form 3:1 complexes with metals, which are overall neutral. Neutral ligands like phenanthroline can be coordinated in addition, because the coordination number of the ions is eight. Among the widely known ligands β–diketone appears to meet the requirements for lanthanide luminescent purpose. The advantage of the use of β–diketone ligands is that they form stable complexes with Ln^{3+}cation.The π–π^*transition of β–diketones is intense and occurs over a significant range of wavelengths that is appropriate for sensitization of Ln^{3+}cation luminescence. The replacement of C–H bonds in a β-diketone by C–F bonds is significant in the design of highly luminescent lanthanide complexes concerned the efficient emission. C–F oscillators lower the vibrational energy of the ligands and decrease the energy loss caused by ligand vibration and thereby enhances the emission intensity of the lanthanide ion. Further due to the heavy-atom effect, which facilitates inter system crossing, the lanthanide–centered luminescent properties are enhanced [4].

These are of special interest in the fabrication of OLED devices because the ternary complexes with phenanthroline or bathophenanthroline have a much lower sublimation point that allows easy sublimation of these materials on OLED devices. The lowered sublimation points are caused by distortion of the symmetry in the complexes and vacuum deposition of the complexes is relatively easily achieved.

2. EXPERIMENTAL

2.1. Materials and Methods

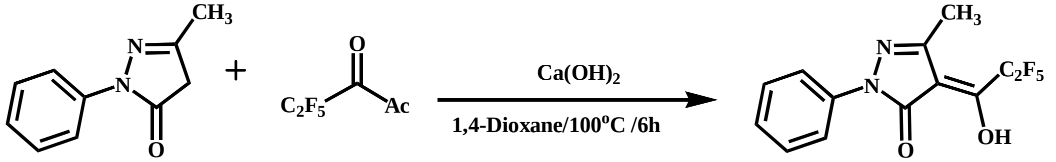
Commercially available chemicals: Europium (III) nitrate fluoropropionate (TCL), 1,10–phenanthroline are used without further purification. Infrared spectra of all samples were performed on KBr pellets in the 4000–400 cm^{-1} region with a resolution of 4 cm^{-1}, by accumulating 64 scans using a Perkin–Elmer Spectrum One FT–IR Spectrometer. A Bruker 300 MHz NMR spectrometer was used to record the ^1H NMR spectrum of the ligands. The excitation and emission spectra of the samples spectra were recorded on a Spex–Fluorolog FL3 22 spectrofluorimeter equipped with a double grating 0.22m Spex 1680 monochromator and a 450W Xe lamp as the excitation source operating in the front face mode.

2.2. Synthesis of the Ligand

Synthesis of 3 – methyl 4-(2,2,3,3,3–penta fluoro–1–hydroxypropylidene)–1–phenyl -1H–pyrazol–5(4H)–one (HMPP)

0.25g (1.435 mmol)1–Phenyl–3-methyl–5–pyrazolone and 0.111g (1.498mmol) calcium hydroxide was taken in a RB flask. It is dissolved in 1,4dioxane (10ml). Heated in a water bath at 60°C for about half an hour. It is cooled and 0.275g (1.432mmol) of ethyl pentafluoropropionate (C_5-$H_5F_5O_2$) was added and stirred for 6 hours. The resulting solution was quenched with water, added 2M HCI, and the solution was extracted twice with chloroform. The organic layer was dried over sodium sulphate (Na_2SO_4), and the solvent was evaporated. The reaction mixture is then purified by chromatography on a silica gel column with mixture of chloroform (20%) and hexane (80%) as the eluent to get the yellow solid as the product. 3–methyl 4–(2,2,3,3,3–pentafluoro–1–hydroxypropylidene)–1–phenyl–1H–pyrazol–5(4H)–one (HL).

^1H NMR ($CDCI_3$) :δ = 7.26–7.86(m, 5H, phenyl); 1.73(s, 3H, CH_3 of the pyrazole ring) (ppm) IR (KBr)ν_{max}: 2929, 1628(C=O), 1597, 1503, 1358, 1213, 749cm^{-1}



Scheme 1: Synthesis of the ligand

2.3. Synthesis of the binary complex

The Eu(III) complex with the ligand **HL** was synthesized according to the following method

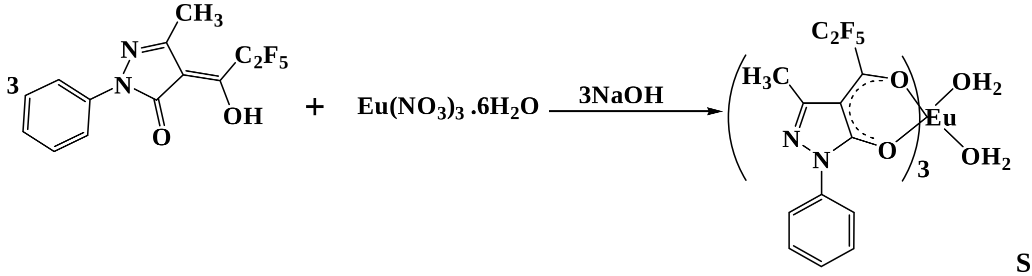
Eu $(L)_3.2H_2O$: An ethanolic solution of $Eu(NO_3)_3.6H_2O$ (0.5 mmol) was added to a solution of HL (1.5 mmol) in ethanol in presence of NaOH (1.5 mmol). Precipitation took place immediately, and the reaction mixture was stirred for 10 hrs at room temperature (Scheme **2**). The product was filtered, washed with ethanol, then with water. The complex was then purified by recrystallization from acetone–water mixture, dried and stored in a desiccator.

IR (KBr) ν_{max}: 3391, 1612, 1577,1484, 1400, 1232, 1154, 757 cm^{-1}.

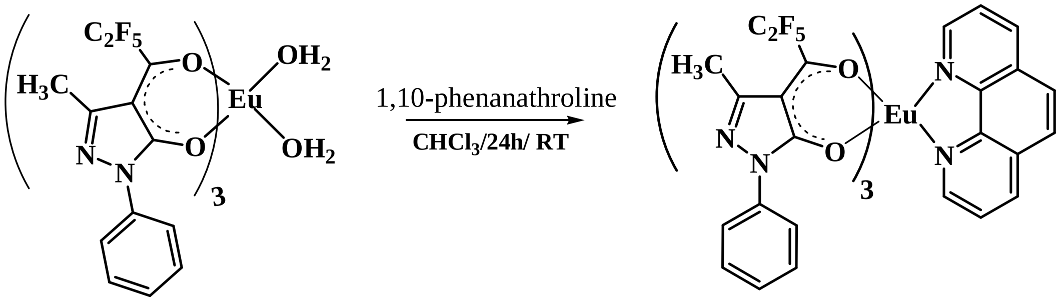
2.4. Synthesis of ternary complex

Synthesis route of the complex is shown in Scheme **3**. The complex was prepared by stirring equimolar solutions of $Eu(L)_3.2H_2O$ and 1,10–phenanathroline in $CHCl_3$ for 24 hrs at room temperature. The product was obtained after solvent evaporation and is purified by recrystallization from chloroform-hexane mixture.

$Eu(L)_3$phen: IR (KBr) ν_{max}: 3065,1641, 1613, 1485, 1439,1316, 1235, 1152, 1053, 757 cm^{-1}.



Scheme 2. Synthesis of binary complex $Eu(L)_3.2H_2O$



Scheme 3: Synthesis of ternary complex $Eu(L)_3$(phen)

3. RESULTS AND DISCUSSIONS

3.1. Synthesis and characterization of the ligand

The ligand HL was prepared as described as in Scheme **1** and was characterized by ^1H NMR. In the^1H NMR spectrum of the ligand, no peak corresponding to the enolic–OH has been observed. However, the absence of a peak at δ 3.4 ppm, corresponding to the methylene proton at the fourth position of the pyrazolone ring, confirms the existence of the ligands in the enolic form.

3.2. Structure and characterization of Europium(III) complex

The synthesis procedure for europium complexeswere shown in Schemes **2** and **3**. The IR spectra of the binary complex show a broad absorption in the region 3000–3500 cm^{-1}, indicating the presence of solvent molecules in the complex. The existence of solvent molecules in lanthanide complexes with β–diketones is well documented [5]. On the other hand, the absence of the broad band in the region 3000–3500 cm^{-1} for the ternary complex, suggests that water molecule has been displaced by the bidentate ligands. The carbonyl stretching frequency of the ligands has been shifted to lower wave numbers in all these complexes indicating the involvement of carbonyl oxygen in the complex formation with Eu^{3+} ion. Red shifts are observed in the C=N of 1,10-phenanthroline in the ternary complexes show the involvement of nitrogen in complex formation with Eu^{3+} ion in these complexes.

3.3. UV–Vis Spectra

UV–Vis absorption spectra of the β-diketone, 1,10–phenanthroline, and their corresponding Eu(III) complexes are measured in CH_3CN ($c=2\times10^{-5}$) are shown in Figure 1. The maximum absorption bands at 288 nm for the ligands **HL** is attributed to singlet–singlet π–π^* enol absorption of β–diketonates. Furthermore, compared with the spectra of the ligands **HL**, the absorption band of the corresponding europium complexes are all red shifted by 2 nm, which is a consequence of the enlargement of the conjugate structure of ligands after coordinating to the Eu^{3+} ion. The spectral shapes of the absorption spectra of Eu(III) complexes in CH_3CN are similar to those of the corresponding ligands, indicating that the coordination of the europium ion does not significantly influence the energy of the singlet state of the β–diketone ligands.

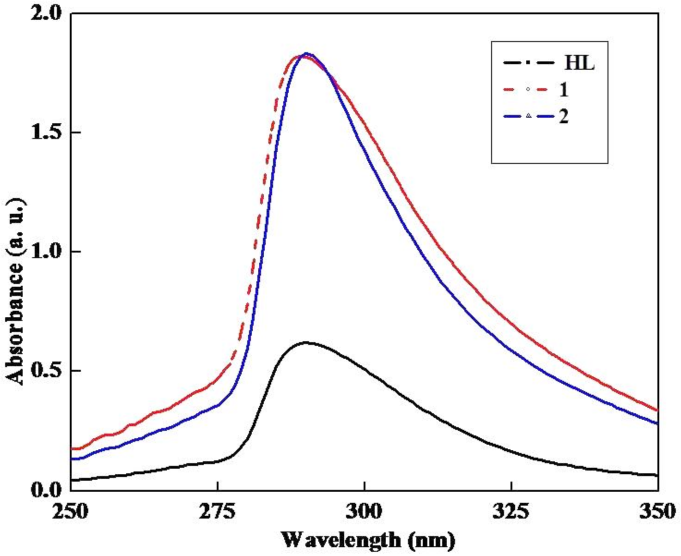


Fig. 1: UV–Visible spectra of **HL** and complexes **1–2** in acetonitrile (c = 2 × 10^{-5} M).

The molar absorption coefficients (ε) of the ligands **HL** is calculated as 2.81×10^4 (288 nm) $Lmol^{-1}cm^{-1}$, revealing that the ligand has a strong ability of absorbing light. Similarly, the determined molar absorption coefficients (ε) of the complexes Eu(**L**)$_3$(H2O)$_2$ and Eu(**L**)$_3$(phen) were 7.6×10^4 (290 nm) L $mol^{-1}cm^{-1}$, which is about three times of those of the corresponding ligand, indicating the presence of three ligands in each complex molecule and is in good agreement.

3.4. PL Properties of Europium (III) Complexes 1–2

The solid state excitation and emission spectra of the europium complexes **1–2**, recorded at 298 were shown in Figure 2. The excitation spectra were obtained with emission monitored at $^5D_0\rightarrow{}^7F_2$ hypersensitive transition around 612 nm. The room temperature excitation spectra of the europium complexes exhibit a broad band between 250 and 450 nm, which can be assigned to $^1\pi$–π^* electron transition of the ligands [6–7].

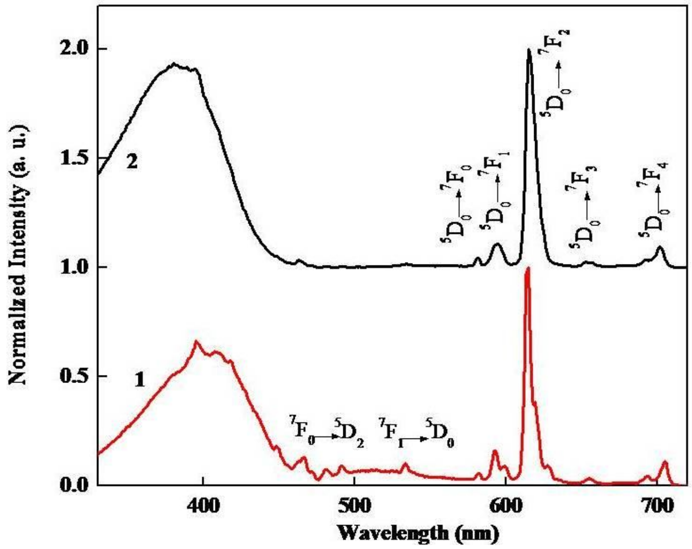


Fig. 2. Room-temperature excitation and emission spectra of complexes **1–2** (λ_{ex}= 380 nm), emission monitered around 613 nm.

The excitation spectra also show a series of narrow bands assigned to the 4f-4f transitions from the $^7F_0$ ground level to the excited states. However, these bands are less intense than those bands corresponding to the $S_0 \rightarrow S_1$ transition of the ligands. This result gives evidence of europium luminescence sensitization through intramolecular energy transfer from the β-diketones. Further, it also proves that luminescence sensitization via excitation of the ligand is much more efficient than the direct excitation of the Eu^{3+} ion absorption level [8]. The normalized photoluminescence spectra of the complexes **1–2** in solid state under the excitation wavelengths that maximize the Eu^{3+} emission intensity are shown in Figure 2. The emission spectra of the complexes display characteristic sharp peaks in the 575-700 nm region associated with the $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions of the Eu^{3+} ion. The five expected peaks of the $^5D_0 \rightarrow {}^7F_{0-4}$ transitions are well resolved, and the hypersensitive $^5D_0 \rightarrow {}^7F_2$transition is very intense, pointing towards a highly polarizable chemical environment around the Eu^{3+} ion, and is responsible for the red emission colour of the complexes. Further, the emission spectra of complexes show only one peak for the $^5D_0 \rightarrow {}^7F_0$, indicating the presence of a single chemical environment around the Eu^{3+} ion and also show that the metal ion occupies a low–symmetry site [9]. It is also important to mention that the emission spectra of the europium complexes do not exhibit ligand centered transitions, indicating that there is an efficient intramolecular energy transfer from the ligands to the Eu^{3+} ion.

3.5. Energy transfer between ligands and Europium(III)

Generally, the sensitization pathway in luminescent europium complexes consist of the excitation of the ligands from the ground state to their excited singlet states, and subsequently through the intersystem crossing of the ligands to their triplet states, following the energy transfer from the triplet state of the ligand to the central ion [10]. In this process, the 4f electrons of the Eu^{3+}ion are excited to the $^5D_0$ manifold ion from the ground state, finally the Eu^{3+}ion emits when the 4f electrons undergo a transition from the excited state of $^5D_0$to the ground state [11].

4. CONCLUSIONS

New pyrazolone based fluorinated ligand, 3–methyl 4–(2,2,3,3,3–penta fluoro–1–hydroxypropylidene)–1–phenyl–1H–pyrazol–5(4H)–onehas been synthesized and well characterized. Europium-containing complexes were synthesized by adduct formation between 3-methyl 4–(2, 2, 3, 3, 3–penta fluoro–1–hydroxypropylidene)–1–phenyl–1H–pyrazol–5(4H)–one and europium (III) complex and a bidentate neutral donor 1,10–phenanthroline (phen). The emission spectra of the complexes display characteristic sharp peaks in the 575–700 nm region associated with the $^5D_0 \rightarrow ^7F_J$ (J = 0–4) transitions of the Eu^{3+} ion. The sensitization mechanism for luminescent europium complexes involves a triplet pathway, in which the transfer of energy absorbed by the ligand to the Eu^{3+} ion takes place from the ligand–centered triplet excited state. The results demonstrate that the substitution of solvent molecules by bidentatephen molecule in $Eu(L)_3(H_2O)_2$greatly enhances the metal–centered luminescence.

REFERENCES

[1] Bünzli, J.–C. G., Chemical Society Reviews, 110, **2010**, 2729–2755.
[2] Binnemans, K., Handbook on the physics and chemistry of rare earths, Elsevier, Amsterdam, 35, **2005,** 107.
[3] Biju, S.; Ambili Raj, D. B.; Reddy, M. L. P.; Kariuki, B. M., Inorganic Chemistry, 45, **2006**, 10651–10660.
[4] Carlos, L. D.; de Mello Donega, C.; Albuquerque, R. Q.; Alves Jr. S.; Menezes, J. F. S.; Malta, O. L. , Molecular Physics, 101, **2003**, 1037–1045.
[5] Eliseeva, S. V.; Kotova, O. V.; Gumy, F.; Semenov, S. N.; Kessler, V. G.; Lepnev, L. S.; Bünzli, J.–C. G.; Kuzmina, N. P. , Journal of Physical Chemistry, 112, **2008**, 3614–3626.
[6] de Sa, G. F.; Malta, O. L.; de Mello Donega, C.; Simas, A. M.; Longo, R. L.; Santa–Cruz, P. A.; da Silva Jr, E. F., Coordination Chemistry Reviews, 196, **2000,** 165–195.
[7] Pavithran, R.; Saleesh Kumar, N. S.; Biju, S.; Reddy, M. L. P.; Alves, Jr. S.; Freire, R. O. , Inorganic Chemistry, 45, **2006,** 2184–2192.
[8] Latva, M.; Takalo, H.; Mukkala, V. M.; Matachescu, C.; Rodriguez–Ubis, J. C.; Kanakare, J., Journal of Luminescence, 75, **1997**, 149–169.
[9] Kai, J.; Parra, F. D.; Brito, H. F., Journal of Materials Chemistry, 18, **2008,** 4549–4554.
[10] Xu, H.; Wang, L.–H.; Zhu, X.–H.; Yin, K.; Zhong, G.–Y.; Hou X.–Y.; Huang, W., Journal of Physical Chemistry B, 110, **2006,** 3023–3029.
[11] Huang, C., Science Press: Beijing, **1997**.