



## Structural and photophysical studies of europium complexes containing triazole ligands

Alexey N. Gusev<sup>a,\*</sup>, Victor F. Shul'gin<sup>a</sup>, Svetlana B. Meshkova<sup>b</sup>, Pavel G. Doga<sup>b</sup>, Miki Hasegawa<sup>c</sup>, Grygory G. Aleksandrov<sup>d</sup>, Igor L. Eremenko<sup>d</sup>, Wolfgang Linert<sup>e,\*</sup>

<sup>a</sup>Taurida National V.I. Vernadsky University, Simferopol 95007, Ukraine

<sup>b</sup>A.V. Bogatsky Physico-chemical Institute of the National Academy of Sciences of Ukraine, Odessa 65080, Ukraine

<sup>c</sup>Department of Chemistry and Biological Science, College of Science and Technology, Aoyama Gakuin University, Kanagawa 252-5258, Japan

<sup>d</sup>N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow 119991, Russia

<sup>e</sup>Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163, A-1060 Vienna, Austria

### ARTICLE INFO

#### Article history:

Received 19 October 2011

Accepted 10 February 2012

Available online 23 February 2012

#### Keywords:

Eu complex

1,2,4-Triazole derivatives

X-ray study

Luminescence

### ABSTRACT

Mono- and bistriazoles ligands have been used to prepare ternary mixed ligand europium(III) complexes in which the remaining ligands are dibenzoylmethane anions (DBM). The complexes were characterized by various measurements including single-crystal X-ray crystallography. Photophysical studies on both ligands and the complexes were carried out. The complexes show strong sharp red emissions in the solid state corresponding to  ${}^5D_0 \rightarrow {}^7F_J$  ( $J = 0-3$ ) with a  ${}^5D_0 \rightarrow {}^7F_2$  (612–613 nm) transition as the most prominent one. It was shown that high thermal stability, luminescence intensity and quantum yield comparable or higher than those for the  $\text{Eu}(\text{DBM})_3\text{Phen}$  makes such complexes a promising material for OLED.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Numerous Eu(III) organic ligand's complexes, especially with a  $\beta$ -diketones are extensively investigated with regard to their intense photoluminescence with narrow spectral band and high quantum yields which can reach 100% in theory [1]. These optical properties are promising for the creation of emitters for OLED [2]. The literature contains many references of creating devices on europium complexes basis with brightness up to  $1000 \text{ cd m}^{-2}$ . Unfortunately high efficiency of these electroluminescent devices has not been achieved so far. One of the important reasons is the poor carrier transporting properties (especially electrons) of these complexes. Unbalanced injection and transport of charge carriers would cause their recombination at locations other than the emitting layer, leading to low OLEDs efficiency and reduced lifetime [3]. There are two main approaches to improve carrier-transporting properties of the europium complexes. The first is doping europium complexes into polymers or small molecular compounds with high hole or electron mobility. The second one is grafting hole- or electron-transporting units on ligands. It is well known that 1,3,4-oxadiazole and 1,2,4-triazole derivatives are the most widely employed as electron-transporting and hole-blocking materials

[4]. Several groups have been focused on the design and synthesis of oxadiazole-functionalized  $\beta$ -diketone ligands and corresponding lanthanide complexes. The literature contains several interesting results which show the effectiveness of such direction of investigation for improving carrier transporting properties of Eu(III) complexes [5]. However, we could not find any mention about employing triazole derivatives as ligands for design luminescent europium complexes. Meanwhile, besides the excellent electron-transporting properties triazoles [6] have high photo- and thermal-stability, which is especially important when creating a thin film OLEDs by vacuum deposition. In this paper we describe the structures and photophysical properties of ternary complexes of ions europium(III) with mixed-ligand donor sets consisting of dibenzoylmethane (the anion – DBM) and mono- and bistriazole (L1–L6, see Fig. 1).

## 2. Results and discussion

### 2.1. Syntheses and characterization

3d-Metal complexes of L1 and L2 were reported in numerous papers [7,8]. Recently, we investigated Zn, Cd, Ag complexes with the ligand L3, and the emission properties of the complexes based on this ligand were reported [9]. Coordination compounds of bistriazole's ligands L4–L6 have not been described in literature to our knowledge.

\* Corresponding authors.

E-mail addresses: [galex0330@rambler.ru](mailto:galex0330@rambler.ru) (A. Gusev), [wlinert@mail.zserv.tuwien.ac.at](mailto:wlinert@mail.zserv.tuwien.ac.at) (W. Linert).

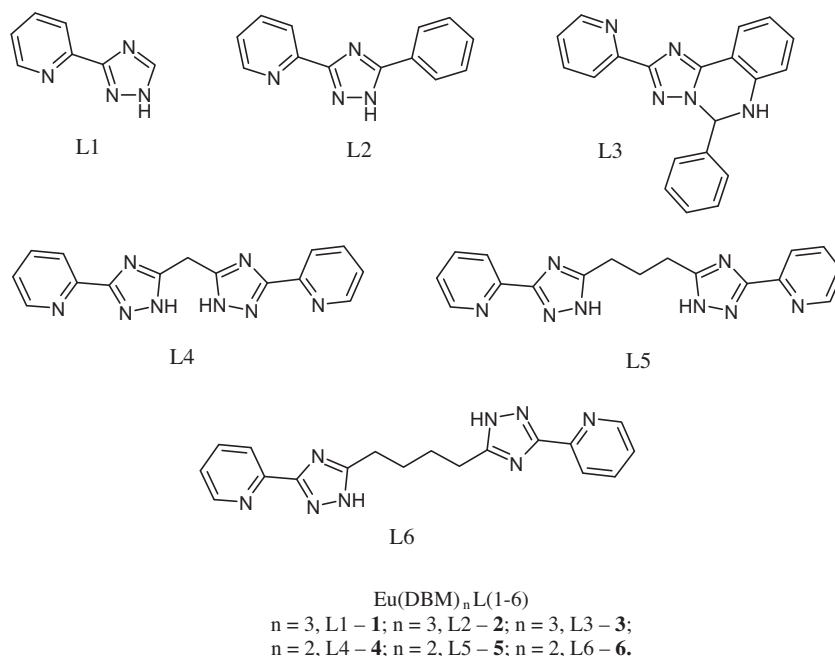


Fig. 1. Molecular structures and abbreviations of the used ligands and complexes.

Investigated complexes **1–6** were prepared in high yields by the reaction of ligands L1–L6 with  $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$ , and were characterized by elemental analyses, IR spectroscopy and X-ray single-crystal diffraction analyses. All complexes are air stable at ambient temperature. Although all the reactions of  $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$  with L1–L6 were carried out under similar conditions in the molar ratio of 1:1, the isolated compounds had different stoichiometry. In the case of monotriazoles ligands L1–L3 reaction proceeds with the substitution of water molecules from  $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$  and the binding of the triazole's unit. Ligands L4–L6 not only replace the water molecules, but one molecule of dibenzoylmethane.

Investigated europium complexes have displayed similar IR spectra. The stretching vibration peaks originating from C=O and C=C, double bonds were observed at  $1595\text{--}1596$  and  $1518\text{ cm}^{-1}$ , respectively. They indicate that bidentate ligand DBM is coordinated with Eu(III) ion. Another binding vibration peak from Eu–N vibrations was also observed at  $511\text{--}516\text{ cm}^{-1}$  together with characteristic vibration peaks of triazoles unit which means that L1–L6 ligands are also binding to europium ion. There is no broad absorption in the region  $3000\text{--}3500\text{ cm}^{-1}$ , indicating that absence of solvent molecules in the complex suggests that water or solvent molecules have been completely replaced by the bi- and tetradentate nitrogen donors.

The absence of solvate molecules in the complexes is confirmed by thermogravimetric analysis too. In the temperature range from 25 to  $260\text{--}390\text{ }^\circ\text{C}$  weight loss is not more than 2%. The thermal stability of the complexes was estimated at the beginning of the thermal oxidative degradation which starts from  $260\text{ }^\circ\text{C}$  ( $\text{Eu}(\text{DBM})_3\text{L1}$ ) to  $390\text{ }^\circ\text{C}$  ( $\text{Eu}(\text{DBM})_3\text{L3}$ ). Decomposition are finished in the range of  $800\text{--}900\text{ }^\circ\text{C}$  for all complexes. This data shows that the thermal stability of the europium complexes is comparable to or even better than the well known  $\text{Eu}(\text{DBM})_3\text{Phen}$  complex [10]. Therefore the introduction of triazoles in the inner coordination sphere can be used to increase the thermal stability of europium complexes.

## 2.2. Structures of complexes

The structures of  $\text{Eu}(\text{DBM})_3\text{L3}$  (**3**) and  $\text{Eu}(\text{DBM})_2\text{L5} \cdot 2\text{C}_6\text{H}_6$  were elaborated by single-crystal X-ray crystallography. Suitable single

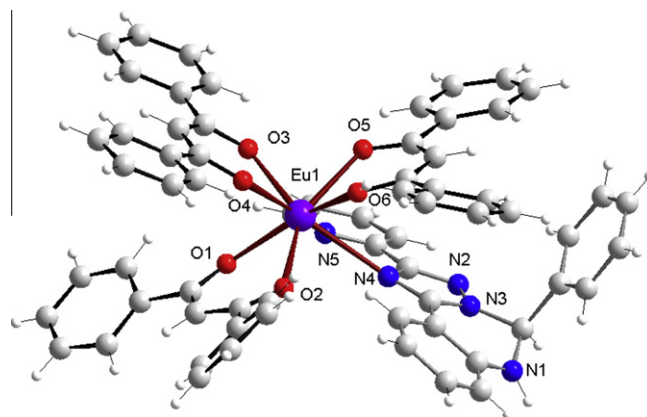


Fig. 2. Structure of the complex  $\text{Eu}(\text{DBM})_3\text{L3}$ . Selected bond lengths (Å) and angles ( $^\circ$ ). Eu1–O4 2.296(5); Eu1–O2 2.326(4); Eu1–O3 2.342(4); Eu1–O6 2.342(5); Eu1–O5 2.373(4); Eu1–O1 2.376(4); Eu1–N5 2.604(5); Eu1–N4 2.705(5); O4–Eu1–O2 75.94(18); O4–Eu1–O3 71.40(16); O2–Eu1–O3 135.13(15); O6–Eu1–O5 70.23(15); O2–Eu1–O1; 72.98(16); N5–Eu1–N4 63.17(16).

crystals were obtained by crystallization procedures indicated in the experimental part. Molecular structure of  $\text{Eu}(\text{DBM})_3\text{L3}$  (**3**) is depicted in Fig. 2.

Complex **3** crystallizes in orthorhombic symmetry with  $P2_12_12_1$  space group. The central Eu(III) ion is coordinated with six oxygen atoms from bidentate DBM ligands and two nitrogen atoms from L3. The coordination geometry of the metal center is best described as approximately square antiprismatic, given the geometric constraints imposed by the bite angles of the chelating ligand, with one square plane defined by O3/O4/O5/O6 (average deviation of these atoms from the best-fit mean plane through them,  $0.073\text{ \AA}$ ) and the other defined by O1/O2/N4/N5 (average deviation of these atoms from the best-fit mean plane through them,  $0.137\text{ \AA}$ ). The square rings are rotated by an angle of around  $82.91^\circ$  with respect to each other. The angle between these two mean planes is  $1.22^\circ$ . The bond length between the europium ion and the oxygen atoms of DBM is varied from 2.296 to  $2.376\text{ \AA}$ . Slight asymmetry is

Download English Version:

<https://daneshyari.com/en/article/1310911>

Download Persian Version:

<https://daneshyari.com/article/1310911>

[Daneshyari.com](https://daneshyari.com)