Inorganica Chimica Acta 386 (2012) 1-7

Contents lists available at SciVerse ScienceDirect

## Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# Two complexes of Eu<sup>3+</sup> ion with pentadentate Schiff-base ligands exhibiting red photoluminescence

### Xu-Sheng Gao\*, Jin-Tang Wang

College of Science, Nanjing University of Technology, Nanjing 210009, PR China

#### ARTICLE INFO

Article history: Received 1 May 2011 Received in revised form 12 February 2012 Accepted 13 February 2012 Available online 20 February 2012

Keywords: Rare earth ion Coordination compound Crystal structure Luminescence property

#### ABSTRACT

Two luminescent europium complexes,  $Eu(DAPBH)_2(NO_3)_3 \cdot 2H_2O$  (1) and  $Eu(DAPBH)(CH_3CH_2OH)$ (SCN)<sub>3</sub>·H<sub>2</sub>O (2) (where DAPBH = (1,1'-(pyridine-2,6-diyl)bis(ethan-1-yl-1-ylidene))dibenzohydrazide, have be synthesized and structurally characterized. The  $Eu^{3+}$  ion is 10-coordinated with six N atoms and four O atoms from two pentadentate DAPBH ligands to form a distorted bicapped tetragonal antiprism geometry and the nitrate counter ions are not coordinated to  $Eu^{3+}$  ion in 1, while the 9-coordinate  $Eu^{3+}$  ion is bound to the N atoms of three monodentate thiocyanates (counter ions), three N atoms and two O atoms of a pentadentate DAPBH ligand as well as to the O atom of an ethanol molecule with a distorted monocapped tetragonal antiprism coordination environment in 2. Two complexes exhibit a red luminescence of  $Eu^{3+}$  ion, stemming from the intra-4f transitions, which is contributed to that (1) the coordination sphere of  $Eu^{3+}$  ion completed by pentadentate DAPBH ligands or counter anions effectively protect the excited state of  $Eu^{3+}$  ion from being quenched by water molecules in 1 and 2; (2) there should be a better match between the pentadentate DAPBH ligand triplet excited state and europium <sup>5</sup>D<sub>0</sub> excited state.

© 2012 Elsevier B.V. All rights reserved.

#### 1. Introduction

The f-f transitions in trivalent rare earth ions, RE<sup>3+</sup>, lead to interesting luminescent properties. These ions have therefore been widely studied for applications such as optical signal amplifiers [1,2], electroluminescent devices [3–9]. Additionally, the 4f orbitals of RE<sup>3+</sup> ion are shielded from the chemical environment by the 5s5p orbitals, which produce very narrow bands in the emission and absorption spectra from the compounds in the gas, solid state or solution phases. This spectroscopic feature makes the RE<sup>3+</sup> ions potential local luminescent probes for diagnostic application in biological systems [10–12]. However, the intraconfigurational 4f–4f transitions are parity forbidden and the corresponding emission and absorption spectra exhibit weak intensity under excitation monitored on the  ${}^{2S+1}L_{I}$  levels of the RE<sup>3+</sup> ion. Fortunately, some organic ligands can act as an 'antenna' (in which ligand possesses the strong absorption bands in the UV or visible range of light), in such a complex there is a better match between the excited states of ligand and  $RE^{3+}$  ion<sup>1</sup>, and the sensitization process via energy transfer between the ligand and RE<sup>3+</sup> ion is much more effective than

the direct excitation of RE<sup>3+</sup> ion [13,14]. Up to date, the varieties of ligands have been developed for this purpose which ranges from simple aromatic acids to more complicated multidentate ligand architectures [15–21].

Amongst the RE<sup>3+</sup> ions, the Eu<sup>3+</sup> ion is a particularly attractive luminescent center and the corresponding complexes generally present red luminescence, and the information about the ligandfield splitting of Eu<sup>3+</sup> ion, the energy transfer processes between the ligands and Eu<sup>3+</sup> ion as well as the quantum efficiency of the emitting levels of Eu<sup>3+</sup> ion can be obtained from the emission and excitation spectra. For a luminescent Eu<sup>3+</sup> complex, the first triplet state of a ligand is usually responsible for most of the energy transfer between the ligand and Eu<sup>3+</sup> ion [22,23], while the singlet-state excitation of a ligand also play non-negligible role in the energy transfer from a ligand to the Eu<sup>3+</sup> luminescent center [24]. On the other hand, the excited state of Eu<sup>3+</sup> ion is effectively quenched by the interactions between the luminescent Eu<sup>3+</sup> center and high energy vibrations like O–H ( $v_{O-H} \approx 3400 \text{ cm}^{-1}$ ) groups in solvent or water as quenchers. Therefore, to achieve a brightly luminescent  $Eu^{3+}$  complex, it is desirable that the use of suitable antenna can completely saturate the coordination sphere of Eu<sup>3+</sup> ion to minimize non-radiative deactivations caused by water molecules or other groups with high energy vibration to bind Eu<sup>3+</sup> ion [25–27]. Accordingly, a multidentate ligand with aromatic groups is probably a better candidate using for constructing luminescent Eu<sup>3+</sup> complex.





<sup>\*</sup> Corresponding author. Tel.: +86 25 83587435; fax: +86 25 58139988. *E-mail address:* gaoxs@njut.edu.cn (X.-S. Gao).

<sup>&</sup>lt;sup>1</sup> *Notes.* Theoretically, the ligand triplet state has to be above and close to the emitting level of the rare earth ion to guarantee an efficient intramolecular energy transfer process.

<sup>0020-1693/\$ -</sup> see front matter @ 2012 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2012.02.021



Scheme 1. Molecular structure of the pentadentate pyridyl-based Schiff-base ligand.

#### Table 1

Crystallographic and structure refinement data for 1 and 2.

Compound	1	2
Formula Formula weight Crystal system	C <sub>46</sub> H <sub>46</sub> EuN <sub>13</sub> O <sub>15</sub> 1172.92 triclinic	C <sub>28</sub> H <sub>29</sub> EuN <sub>8</sub> O <sub>4</sub> S <sub>3</sub> 789.73 monoclinic
Space group	PĪ	P2(1)/c
Unit cell dimensions		
a (Å)	11.6539(11)	9.5642(10)
b (Å)	12.0889(14)	10.9870(11)
<i>c</i> (Å)	19.609(2)	32.191(3)
α (°)	99.69(3)	90
β (°)	95.34(3)	102.388(3)
γ (°)	106.80(3)	90
V (Å <sup>3</sup> ), Z	2577.5(5), 2	3303.9(6), 4
D <sub>calc</sub>	1.511	1.588
$\mu (\mathrm{mm}^{-1})$	1.296	2.134
F(000)	1192	1584
Unique reflections	10103	5795
Parameters	612	400
Good-of-fit (GOF)	1.168	0.606
$R_1 \left[ I > 2\sigma(I) \right]$	0.0766	0.0522
wR <sub>2</sub>	0.1977	0.0671

 $R_1 = \Sigma(||F_0| - |F_c||) / \Sigma |F_0|, \ wR_2 = \Sigma w(|F_0|^2 - |F_c|^2)^2 / \Sigma w(|F_0|^2)^2]^{1/2}.$ 

We have synthesized a pentadentate pyridyl-based Schiff-base ligand (Scheme 1), and further prepared two complexes of Eu<sup>3+</sup> with this ligand. Herein, we present the crystal structures and photoluminescence properties of those complexes.

Table 2			
Geometric parameters of coordination p	olyhedron in tl	he crystal (	of 1.

Bond lengths (Å)						
Eu1-01	2.423(6)	Eu1-02	2.473(6)	Eu1-03	2.494(6)	
Eu1-04	2.445(6)	Eu1-N2	2.606(8)	Eu1-N3	2.656(7)	
Eu1-N4	2.572(8)	Eu1-N7	2.605(8)	Eu1-N8	2.696(7)	
Eu1-N9	2.575(8)					
Bond angles (	°)					
01-Eu1-02	116.0(2)	01-Eu1-03	81.7(2)	01-Eu1-04	130.2(2)	
01-Eu1-N2	61.1(2)	01-Eu1-N3	115.9(2)	01-Eu1-N4	155.5(2)	
01-Eu1-N7	82.7(2)	01-Eu1-N8	67.6(2)	01-Eu1-N9	75.0(2)	
02-Eu1-03	129.1(2)	02-Eu1-04	84.1(2)	02-Eu1-N2	72.3(2)	
02-Eu1-N3	65.4(2)	02-Eu1-N4	85.2(2)	02-Eu1-N7	158.9(2)	
02-Eu1-N8	115.8(2)	02-Eu1-N9	60.7(2)	03-Eu1-04	121.8(2)	
03-Eu1-N2	77.8(2)	03-Eu1-N3	64.0(2)	03-Eu1-N4	74.8(2)	
03-Eu1-N7	60.4(2)	04-Eu1-N8	62.7(2)	04-Eu1-N9	77.9(2)	
N2-Eu1-N3	59.7(2)	N2-Eu1-N4	119.4(2)	N2-Eu1-N7	128.1(3)	
N2-Eu1-N8	124.5(2)	N2-Eu1-N9	87.2(3)	N3-Eu1-N4	59.7(3)	
N3-Eu1-N7	117.2(2)	N3-Eu1-N8	175.7(2)	N3-Eu1-N9	123.1(2)	
N4-Eu1-N7	79.4(3)	N4-Eu1-N8	116.0(3)	N4-Eu1-N9	128.8(3)	
N7-Eu1-N8	60.1(3)	N7-Eu1-N9	119.6(3)	N8-Eu1-N9	59.5(2)	
04-Eu1-N2	156.1(2)	03-Eu1-N8	115.1(2)	03-Eu1-N9	156.4(2)	
04-Eu1-N7	75.7(2)	04-Eu1-N3	113.9(2)	04-Eu1-N4	60.5(2)	
N2-EUI-N3 N2-EU1-N8 N3-EU1-N7 N4-EU1-N7 N7-EU1-N8 O4-EU1-N2 O4-EU1-N7	55.7(2) 124.5(2) 117.2(2) 79.4(3) 60.1(3) 156.1(2) 75.7(2)	N2-EU1-N4 N2-Eu1-N9 N3-Eu1-N8 N4-Eu1-N8 N7-Eu1-N9 O3-Eu1-N8 O4-Eu1-N3	119.4(2) 87.2(3) 175.7(2) 116.0(3) 119.6(3) 115.1(2) 113.9(2)	N2-EUI-N7 N3-Eu1-N4 N3-Eu1-N9 N4-Eu1-N9 N8-Eu1-N9 O3-Eu1-N9 O4-Eu1-N4	128.1(3) 59.7(3) 123.1(2) 128.8(3) 59.5(2) 156.4(2) 60.5(2)	

#### 2. Experimental

#### 2.1. Chemicals and solvents

All chemicals and solvents were of reagent grade and used without further purification.

#### 2.2. Materials

The Schiff-base ligand (1,1'-(pyridine-2,6-diyl)bis(ethan-1-yl-1-ylidene))dibenzohydrazide (abbr. DAPBH), was prepared following the reported procedure [28]. Element analysis of C, H and N. *Anal.* Calc. for C<sub>23</sub>H<sub>21</sub>N<sub>5</sub>O<sub>2</sub>: C, 69.07; H, 5.54; N, 17.35. Found: C, 69.17; H, 5.26; N, 17.54%. IR spectrum (KBr disc, cm<sup>-1</sup>): 3449 for v(N—H), 1663 for v(C=O), 1612 and 1567 for v(C=N) and v(C=C). 1H NMR data (300 MHz, DMSO, 25 °C, TMS):  $\delta$  = 7.51–7.91 (m, 13 H, H<sub>phenylring</sub>), 2.54 (s, 6 H, H<sub>methylgroup</sub>), 10.89 (s, 2 H, H<sub>aminogroup</sub>) ppm.

#### 2.3. Chemical and physical characterizations

C, H and N microanalyses for complexes **1** and **2** were carried out with a Perkin–Elmer 240 elemental analyzer. FTIR spectra were



Fig. 1. (a) Molecular structure of 1 (uncoordinated NO<sub>3</sub><sup>-</sup> ions, H<sub>2</sub>O molecules and all H-atoms in DAPBH ligands omitted for clarity) and (b) the bicapped tetragonal antiprism coordinated environment of Eu<sup>3+</sup> ion.



Fig. 2. H-bonding interactions in the crystal of 1 (methyl groups, phenyl rings in the penta-dentate ligands and all H-atoms omitted for clarity).

 Table 3

 H-bond interactions in the crystal of 1

in bolid interactions in the crystal of 1.						
D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	∠D–H…A (°)		
N1-H1A012	0.86	1.98	2.764(14)	150.9		
N5-H5A…07	0.86	2.47	3.026(15)	123.1		
N5-H5A…O8	0.86	2.41	2.992(15)	125.4		
N6-H6A…O10	0.86	2.03	2.804(14)	149.3		
N10-H10AOW1	0.86	2.08	2.791(14)	139.6		
OW1-HW1B…OW2	0.85	2.56	2.77(3)	94.8		
OW2-HW2B-06#1	0.85	2.68	3.04(3)	107.2		

Symmetric code: #1 = 1 - x, -y, -z.

recorded using KBr disc on an AVATAR-360 spectrophotometer in the range of 4000–400 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra for the Schiff-base ligand was recorded on an AVANCE-300 spectrometer operating at 300 MHz in DMSO-d<sub>6</sub>. The chemical shifts were measured with respect to internal standard TMS. Emission spectra were recorded using a Hitachi F4500 spectrometer at room temperature. The photoluminescence lifetime was measured with an Edinburgh Instruments FLS920P fluorescence spectrometer. The image of luminescence microscopy of **2** was taken by an OLYMPUS BX51 inverted luminescence microscope under an excitation of green light.

#### 2.4. Preparation of 1

0.2112 g (0.6 mmol) Eu<sub>2</sub>O<sub>3</sub> was dissolved in concentrated HNO<sub>3</sub>; the solution was evaporated to remove the excess HNO<sub>3</sub> and water. The residual solids were dissolved in 25 mL 95% ethanol, and 0.4994 g (1.25 mmol) DAPBH ligands were then added to the above ethanol solution. The mixture was stirred at 55 °C for 3 h and the yellowish solids precipitated upon cooling, then was filtered out and washed with 10 mL absolute ethanol and dried in air yielding 0.53 g (~70% and calculation based on the reactant DAPBH) of **1**. *Anal.* Calc. for C<sub>46</sub>H<sub>46</sub>EuN<sub>13</sub>O<sub>15</sub>: C, 47.10; H, 3.95; N, 15.52. Found: C, 47.24; H, 3.99; N, 15.41%. The main vibration bands in IR spectrum (KBr disc, cm<sup>-1</sup>): 1602s contributed from v(C=O), 1570s assigned to v(C=N), 1545s arose from v(C=C), 1317s given from v(NO<sub>3</sub><sup>-</sup>).

Single crystals of **1**,  $Eu(DAPBH)_2(NO_3)_3 \cdot 2H_2O$ , suitable for X-ray diffraction studies were obtained by slowly evaporating 95% ethanol solution of **1** at room temperature over 3 days.

#### 2.5. Preparation of 2

0.2112 g (0.6 mmol) Eu<sub>2</sub>O<sub>3</sub> was dissolved in concentrated HNO<sub>3</sub>; the solution was evaporated to remove water and excess HNO<sub>3</sub> giving colorless solids, which were mixed with 0.035 g



Fig. 3. (a) Molecular structure of 2 (uncoordinated H<sub>2</sub>O molecule and all H-atoms omitted for clarity) and (b) the monocapped tetragonal antiprism coordination geometry of Eu<sup>3+</sup> ion (viewed along the direction of Eu1–N2 bond).

(0.36 mmol) KSCN in 20 mL absolute ethanol and stirred. The precipitated KNO<sub>3</sub> was removed by filtration, then a solution of 0.4994 g (1.25 mmol) DAPBH in 25 mL 95% ethanol was added dropwisely. This mixture was stirred at 55 °C for 3 h to yield a yellowish solids, which were separated via filtration, washed with 10 mL absolute ethanol and dried in air yielding 0.79 g (~80% and calculation based on the reactant DAPBH) of **2**. Anal. Calc. for C<sub>28</sub>H<sub>29</sub>EuN<sub>8</sub>O<sub>4</sub>S<sub>3</sub>: C, 42.6; H, 3.70; N, 14.2. Found: C, 42.2; H, 3.43; N, 13.9%. The main vibration bands in IR spectrum (KBr disc, cm<sup>-1</sup>): 1600s contributed from v(C=O), 1576s assigned to v(C=N), 1541s arose from v(C=C), 2053s given from v(SCN<sup>-</sup>).

Single crystals of **2**,  $Eu(DAPBH)(SCN)_3 \cdot H_2O$ , suitable for X-ray analysis were obtained by slowly cooling the hot filtrate.

#### 2.6. X-ray crystallography

Single crystal X-ray diffraction data of **1** and **2** were collected on a Siemens SMART-CCD and Enraf–Nonius CAD-4 diffractometer with graphite monochromatic MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K, respectively. The structures were solved by direct methods and refined on  $F^2$  using full matrix least-squares methods with SHELXTL version 97 [29]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were theoretically added, riding on their parent atoms. During the structural refinement of **1**, the geometric constraints were applied to two of three nitrates, N(11)O(5)O(6)O(7) and N(13)O(11)O(12)O(13), respectively. Crystallographic and structural refinement data of **1** and **2** are summarized in Table 1.

#### 3. Results and discussion

#### 3.1. Description of the structures

Complex **1** crystallized in triclinic space group  $P\bar{1}$ , and an asymmetric unit contains one Eu<sup>3+</sup> ion, two DAPBH ligands and three uncoordinated nitrates together with two lattice water molecules. As shown in Fig. 1a, the Eu<sup>3+</sup> ion in the coordination cation is surrounded by two pentadentate DAPBH ligands and coordinated by six N atoms and four O atoms; the bond lengths and angles in the coordination sphere, listed in Table 2, are normal. The coordination geometry of the Eu<sup>3+</sup> ion can be described as a distorted bicapped tetragonal antiprism (Ref. Fig. 1b). Two deformed tetragonal faces of the bicapped tetragonal antiprism, comprised respectively of O(1)N(7)O(4)N(9) and O(2)N(2)O(3)N(4), make a dihedral angle of 2.3° and are nearly parallel to each other. Two O atoms in each tetragonal face occupy trans-sites with the angles

of  $\angle O(1)Eu(1)O(4) = 130.2^{\circ}$  and  $\angle O(2)Eu(1)O(3) = 129.1^{\circ}$ . Two N atoms, labeled as N(3) and N(8), are respectively capped on two tetragonal faces, and the N(3), Eu(1) and N(8) atoms show almost linear arrangement with an angle of  $\angle N(3)Eu(1)N(8) = 175.7^{\circ}$ .

Each DAPBH ligand is hydrogen bonded to three uncoordinated nitrates as well as one of two co-crystallized water molecules. Three crystallographically inequivalent nitrates exhibit distinct hydrogen bonding models. The nitrate with N(12) atom acts as a  $\mu_2$ -bridge linking two DAPBH ligands via N atoms of =N—NH— groups and O atoms of the nitrate with  $d_{O(8)}\cdots_{N(5)}$  = 2.991 Å,  $\angle N(5)$ -H(5A) $\cdots$ O(8) = 125.4° and  $d_{O(10)}\cdots_{N(6)}$  = 2.805 Å,  $\angle N(6)$ -H(6A) $\cdots$ O(10) = 149.3°. The nitrate with N(11) exhibits another  $\mu_2$ -bridge model. O(7) is linked to N(5) of =N—NH— group with  $d_{O(7)}\cdots_{N(5)}$  = 2.991 Å,  $\angle N(5)$ -H (5A) $\cdots$ O(7) = 123.1° and the O(6) atom is connected to Ow(2) with  $d_{O(6)}\cdots_{OW(2)}$  = 3.038 Å,  $\angle Ow(2)$ -Hw(2B) $\cdots$ O(6) = 107.1°. The nitrate with N(13) is attached to the DAPBH ligand via H-bonding interaction between its O atom and the N atom of =N—NH— group with  $d_{O(12)}\cdots_{N(1)}$  = 2.763 Å,  $\angle N(1)$ -H(1A) $\cdots$ O(12) = 123.7°.

As illustrated in Fig. 2, two neighboring coordination cations of  $Eu^{3+}$ , four lattice water molecules together with two nitrates form supramolecular ring architecture through intermolecular H-bonding interactions. And the neighboring supramolecular rings further link into a supramolecular H-bonding chain through two Ow(1)-type water molecules along the *b*-axis direction, and the supramolecular H-bonding chains are held together by means of weak van der Waals forces. The intermolecular H-bond geometric parameters are summarized in Table 3.

Complex **2** crystallizes in the monoclinic space group P2(1)/c, and the asymmetric unit consists of one neutral mononuclear Eu<sup>3+</sup> complex together with one lattice water molecule. The Eu<sup>3+</sup> ion is coordinated by six N atoms and three O atoms from one pentadentate DAPBH ligand, three SCN<sup>-</sup> ions and one ethanol molecule (Ref. Fig. 3a) and shows the coordination geometry with a distorted monocapped tetragonal antiprism (Fig. 3b). The Eu-N bond lengths between Eu<sup>3+</sup> ion and the pentadentate DAPBH ligand range from 2.601 to 2.646 Å with an average value of 2.619 Å, which are comparable to the corresponding values in 1; the Eu–N bond lengths between  $Eu^{3+}$  ion and three SCN<sup>-</sup> anions are in the range of 2.413–2.482 Å, obviously shorter than those between Eu<sup>3+</sup> and pentadentate DAPBH ligand, indicating the existence of stronger Eu-N coordinated bonds between the Eu<sup>3+</sup> ion and the negatively-charged SCN<sup>-</sup> ions than the neutral N atoms. The DAPBH Eu–O distances are 2.419 and 2.431 Å while the ethanol Eu-O distance is 2.426 Å (see Table 4). Two deformed tetragonal faces in the monocapped tetragonal antiprism, comprised respectively of N(4)N(7)O(3)O(2) (the bottom of the tetragonal antiprism) and N(1)N(8)O(1)N(6) (the top of the tetragonal

Table 4 Geometric parameters of coordination polyhedron in the crystal of 2. Bond lengths (Å) F111-01 2.419(6)Fu1-02 2.431(6)Fu1-03 2.426(6)Eu1-N1 2.611(7) Eu1-N2 2.646(6) Eu1-N4 2.601(7) Eu11-N6 2.424(8) Eu1-N7 2.482(6) Eu1-N8 2.413(8) Bond angles (°) 01-Eu1-02 106.88(19) 01-Eu1-03 69.0(2) 01-Eu1-N1 119.3(2) 01-Eu1-N2 60.4(2)01-Eu1-N4 150.7(2)01-Eu1-N6 76.1(2) 01-Eu1-N7 01-Eu1-N8 141.0(2) 81.6(2)  $02 - E_{11} - 03$ 670(2)02-Eu1-N1 121.6(2) 02-Eu1-N2 154.2(2)02-Eu1-N4 61.9(2)02-Eu1-N6 77.0(2) 02-Eu1-N7 72.7(2) 02-Eu1-N8 137.6(2)

03-Eu1-N2

03-Eu1-N7

N1-Eu1-N4

N1-Eu1-N8

121.0(2)

75.8(2)

60.2(2)

85.2(2)

03-Eu1-N4

03-Eu1-N8

N1-Eu1-N6

N2-Eu1-N4

122.2(2)

78.6(3)

81.4(2)

116.8(2)



**Fig. 4.** Hydrogen bonding interactions between the lattice water molecules and the coordinated ethanol molecules and between the lattice water molecules and the S(2)-type SCN<sup>-</sup> anions give rise to a one-dimensional chain along the crystallographic *b*-axis direction.

Table 5					
H-bond	interactions	in	the	crystal	of 2

03-Eu1-N1

03-Eu1-N6

N1-Eu1-N2

N1-Eu1-N7

N2-Eu1-N6

160.6(2)

118.0(3)

60.0(2)

89.9(2)

78.0(2)

	, <b>,</b>	-		
D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	∠D-H…A (°)
03–H3A…04#1 03–H3A…N7 04–H4B…S2#2	0.85 0.85 0.85	2.08 2.58 2.56	2.742(8) 3.015(9) 3.236(8)	134.6 113.2 137.3

Symmetric codes: #1 = x - 1, y, z; #2 = -x + 1, y + 1/2, -z + 1/2.

antiprism) are nearly parallel with a dihedral angle of  $2.39^{\circ}$ . Three coordinated O atoms (O(1), O(2) and O(3)) with N(6) atoms form a side face of the tetragonal antiprism, and the N(2) atom is capped on the top of the tetragonal antiprism. Geometric parameters in the monocapped tetragonal antiprism shaped coordination sphere are listed in Table 4.

As depicted in Fig. 4, the lattice water molecules connect the O atoms of the coordinated ethanol molecules as well as the S(2) atoms of thiocyanates from the neighboring neutral complexes into hydrogen-bonded supramolecular chain along the crystallographic *b*-axis direction. The hydrogen bond geometric parameters





**Fig. 5.** Excitation and emission spectra of (a) **1** and (b) **2** in solid state recorded at room temperature; (c) image of luminescence microscopy of **2** under an excitation of green light.

are summarized in Table 5. There only are van der Waals forces between the neighboring hydrogen-bonded supramolecular chains.

#### 3.2. Solid-state photoluminescence spectra

For the emission spectrum of the Eu<sup>3+</sup> ion, the main emitting level (<sup>5</sup>D<sub>0</sub>) is non-degenerate, thus the split of the emission bands assigned to the transitions from <sup>5</sup>D<sub>0</sub> to <sup>7</sup>F<sub>J</sub> ( $0 \le J \le 4$ ) can provide the information about the local symmetry of the Eu<sup>3+</sup> ion. For example,



Fig. 6. Typical luminescence decay profiles (black lines) observed for (a) 1 and (b) 2 in the solid state at room temperature, and the red lines are the corresponding monoexponential fits of 1 and 2, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the intensity of the  ${}^5D_0 \rightarrow {}^7F_1$  transition is not influenced greatly by the chemical environment because this transition is allowed by the magnetic dipole mechanism; however, the  ${}^5D_0 \rightarrow {}^7F_2$  transition is hypersensitive to the chemical environment around the Eu $^{3+}$  ion. Therefore, the relative intensity between the  ${}^5D_0 \rightarrow {}^7F_2$  and  ${}^5D_0 \rightarrow {}^7F_1$  transitions is a probe for the local symmetry of the Eu $^{3+}$  ion coordination sphere [30,31].

The emission and excitation spectra of 1 and 2 in solid state shown in Fig. 5 were recorded at room temperature. The emission spectrum of 1 under excitation at 362 nm exhibits the characteristic luminescence of Eu<sup>3+</sup> ion, four emission bands, attributed to the transitions of  $Eu^{3+}$  ion of  ${}^5D_0 \rightarrow {}^7F_1$ ,  ${}^5D_0 \rightarrow {}^7F_2$ ,  ${}^5D_0 \rightarrow {}^7F_3$  and  ${}^5D_0 \rightarrow {}^7F_4$ , are respectively centered at 591, 617, 686 and 722 nm; while the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition is not observed, the ratio of the integrated intensities of the  ${}^5D_0 \rightarrow {}^7F_2$  to  ${}^5D_0 \rightarrow {}^7F_1$  transitions (localized at about 623 and 592 nm, respectively) is around 6.9. which indicates the  $Eu^{3+}$  ion coordination environment is asymmetric, in agreement with the crystal structure analyses. The excitation spectrum of **1** in the solid state was measured in the range of 300-450 nm from the emission of the hypersensitive  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition at 617 nm, and presents a broad band between 320 and 400 nm. The characteristic emissions of Eu<sup>3+</sup> ion corresponding to the transitions from  ${}^{5}D_{0}$  to  ${}^{7}F_{l}$  ( $0 \leq l \leq 4$ ) were observed under excitation at 395 nm for 2, and the image of luminescence microscopy of 2 under an excitation of green light, showing red luminescence, is displayed in Fig. 5c. By comparison, the main differences between the emission spectra of two complexes involve the following: (1) the emission band arising from the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition appears at 580 nm for **2** even if its intensity is lower but not for 1; (2) the bands splitting is more remarkable in **2** than in **1** (the  ${}^5D_0 \rightarrow {}^7F_1$ ,  ${}^5D_0 \rightarrow {}^7F_2$  and  ${}^5D_0 \rightarrow {}^7F_4$ transitions split into two bands (590 and 595 nm), two bands (613 and 620 nm) and three bands (686, 694 and 700) nm, respectively, in the emission spectrum of 2); (3) the ratio of the integrated intensities of the  ${}^5D_0 \rightarrow {}^7F_2$  to  ${}^5D_0 \rightarrow {}^7F_1$  transitions is ca. 2.4 in **2**, which is smaller than that (6.9) in **1**; (4) the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transition in 2 shows more than 20 nm blue-shift compared with the corresponding emission band in 1. Obviously, these differences between the emission spectra of 1 and 2 result from the coordination environment distinctions of Eu<sup>3+</sup> ion in two complexes.

The fluorescence lifetime,  $\tau$ , of two complexes are investigated in the solid state at room temperature, and the curves of fluorescence decay of **1** and **2** are illustrated in Fig. 6. The process of fluorescence decay for both **1** and **2** follows a single exponential decay law, as a result, the equation intensity =  $A_0 + A_1 \times \exp(-t/\tau)$  was utilized for fitting the curves of fluorescence decay of **1** and **2**, which gave the best parameters  $A_0 = 11(1)$ ,  $A_1 = 5018(309)$  and  $\tau$  = 5.1(1) ms with an overall  $R^2$  of 0.9499, for **1** versus  $A_0$  = 1.6(9), i<sub>1</sub> = 1805(6) and  $\tau$  = 105(1) ms with an overall  $R^2$  of 0.9979 for **2**. The f-f electronic transitions of lanthanide are forbidden, leading to long excited state decay time.

In addition, the Schiff-base ligand shows weak emission, excited by UV light, in the solid state at ambient temperature, but this weak emission based on the ligand was not observed in the emission spectra of two complexes (Ref. Fig. S3), indicating the existence of efficient energy transfer between the Schiff base ligands and Eu<sup>3+</sup> ion.

#### 4. Conclusion

In summary, a neutral pentadentate DAPBH ligand and two corresponding  $Eu^{3+}$  ion complexes have been synthesized and characterized, respectively. The binding ability of the counter anion to  $Eu^{3+}$  ion influences the components of the complex as well as the coordination environments of  $Eu^{3+}$  ion. Under the same reaction condition, **1** possesses a molar ratio of DAPBH: $Eu^{3+} = 2:1$  and the nitrates with weak binding ability are not coordinated to  $Eu^{3+}$  ion when  $Eu(NO_3)_3$  is the  $Eu^{3+}$  source, while **2** has a molar ratio of DAP-BH: $Eu^{3+} = 1:1$  and the thiocyanates with strong binding ability are coordinated to  $Eu^{3+}$  ion when  $Eu(SCN)_3$  is used as  $Eu^{3+}$  ion resource. The coordination geometry of  $Eu^{3+}$  ion is a bicapped tetragonal antiprism and its 10 coordination atoms are from two pentadentate DAPBH ligands in **1**, whereas a monocapped tetragonal antiprism and its 9 coordination atoms are from one pentadentate DAPBH ligand, three thiocyanates and one ethanol molecule in **2**.

Both 1 and 2 emit the red luminescence of  $Eu^{3+}$  ion, which demonstrates that the pentadentate DAPBH ligand is an efficient antenna for  $Eu^{3+}$  emission.

#### Acknowledgments

Gao thanks Nanjing University of Technology for financial support and Prof. X.M. Ren for his helpful discussion.

#### Appendix A. Supplementary material

Supplementary material CCDC 772925 and 783943 contains the supplementary crystallographic data for the complexes **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2012.02.021.

#### References

- D. Ananias, M. Kostova, F.A.A. Paz, A.N.C. Neto, R.T. De Moura Jr., O.L. Malta, L.D. Carlos, J. Rocha, J. Am. Chem. Soc. 131 (2009) 8620.
- [2] X. Wang, X.G. Kong, Y. Yu, Y.J. Sun, H. Zhang, J. Phys. Chem. C 111 (2007) 15119.
   [3] J. Kido, Y. Okamoto, Chem. Rev. 102 (2002) 2357.
- [4] M. Sun, H. Xin, K.Z. Wang, Y.A. Zhang, L.P. Jin, C.H. Huang, Chem. Commun. (2003) 702.
- [5] H. Xin, F.Y. Li, M. Shi, Z.Q. Bian, C.H. Huang, J. Am. Chem. Soc. 125 (2003) 7166.
- [6] N. Zhao, S.P. Wang, R.X. Ma, Z.H. Gao, R.F. Wang, J.J. Zhang, J. Alloys Compd. 463 (2008) 338.
- [7] S.V. Eliseeva, J.C.G. Bünzli, Chem. Soc. Rev. 39 (2010) 189.
- [8] L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini, E. Tondello, Coord. Chem. Rev. 254 (2010) 487.
- [9] K. Binnemans, Chem. Rev. 109 (2009) 4283.
- [10] I. Hemmilá, V.-M. Mukkala, Crit. Rev. Clin. Lab. Sci. 38 (2001) 441.
- [11] S. Pandya, J.H. Yu, D. Parker, Dalton Trans. (2006) 2757.
- [12] C.H. Song, Z.Q. Ye, G.L. Wang, J.L. Yuan, Y.F. Guan, Eur. J. Chem. 16 (2010) 6464.
- [13] N. Sabatini, M. Guardigli, J.M. Lehn, Coord. Chem. Rev. 123 (1993) 201.
- [14] A.P.S. Samuel, J.L. Lunkley, G. Muller, K.N. Raymond, Eur. J. Inorg. Chem. (2010) 3343.
- [15] G.X. Liu, Y.Y. Xu, X.M. Ren, S.I. Nishihara, R.Y. Huang, Inorg. Chim. Acta 363 (2010) 3727.

- [16] G.J. He, D. Guo, C. He, X.L. Zhang, X.W. Zhao, C.Y. Duan, Angew. Chem., Int. Ed. 48 (2009) 6132.
- [17] X. Zhu, C. He, D.P. Dong, Y. Liu, C.Y. Duan, Dalton Trans. 39 (2010) 10051.
- [18] S. Viswanathan, A. de Bettencourt-Dias, Inorg. Chem. 45 (2006) 10138.
- [19] A.S. Chauvin, F. Gumy, D. Imbert, J.C.G. Bünzli, Spectrosc. Lett. 37 (2004) 517.
   [20] C. Piguet, J.C.G. Bünzli, Chem. Soc. Rev. 28 (1999) 347.
- [21] X.Q. Song, W.S. Liu, W. Dou, Y.W. Wang, J.R. Zheng, Z.P. Zang, Eur. J. Inorg.
- Chem. (2008) 1901.
- [22] S. Sato, M. Wada, Bull. Chem. Soc. Jpn. 43 (1970) 1955.
- [23] M. Latva, H. Takalo, V.M. Mukkala, C. Matachescu, J.C. Rodriguez-Ubis, J. Kankare, J. Lumin. 75 (1997) 149.
- [24] M.H. Ha-Thi, J.A. Delaire, V. Michelet, I. Leray, J. Phys. Chem. A 114 (2010) 3264.
   [25] A. Bellusci, G. Barberio, A. Crispini, M. Ghedini, M.L. Deda, D. Pucci, Inorg. Chem. 44 (2005) 1818.
- [26] A. Beeby, I.M. Clarkson, R.S. Dickins, S. Faulkner, D. Parker, L. Royle, A.S. de Sousa, J.A.G. Williams, M. Woods, J. Chem. Soc., Perkin Trans. 2 (1999) 493.
- [27] J. Yang, Q. Yue, G.D. Li, J.J. Cao, G.H. Li, J.S. Chen, Inorg. Chem. 45 (2006) 2857.
- [28] T.J. Giordano, G.J. Palenik, R.C. Palenik, D.A. Sullivan, Inorg. Chem. 18 (1979) 2445.
- [29] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997.
- [30] E.W.J.L. Omen, A.M.A. van Dongen, J. NonCryst. Solids 111 (1989) 205.
- [31] S. Bucella, P. Riello, B.F. Scremin, P. Calvelli, R. Polloni, A. Speghini, M. Bettinelli, A. Benedetti, Opt. Mater. 27 (2004) 249.