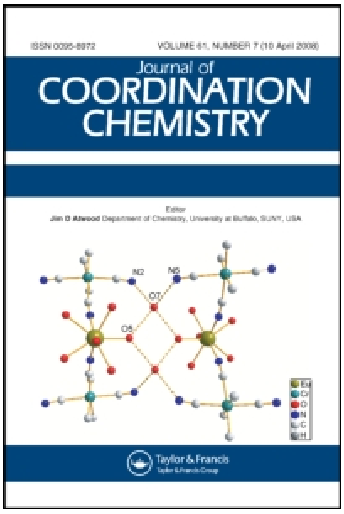

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Structures and fluorescence of two new hetero-dinuclear lanthanide(III) complexes derived from a Schiff-base ligand

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Structures and fluorescence of two new hetero-dinuclear lanthanide(III) complexes derived from a Schiff-base ligand

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Two isostructural dinuclear lanthanide(III)/Schiff-base complexes $[\{Ce_{1.5}Eu_{0.5}(clapi)\}_2]\cdot 2CH_3CN$ (**1**) and $[\{La_{1.5}Eu_{0.5}(clapi)\}_2]\cdot 2CH_3CN$ (**2**) $\{H_3clapi = $ 2-(5-chloride-2-hydroxyphenyl)-1,3-bis[4-(5-chloride-2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine$\}$ have been prepared by template procedure and characterized by elemental analyses, ICP, IR, and single-crystal X-ray diffraction analyses. Lanthanide ions Ce(III) and Eu(III) in **1**, and La(III) and Eu(III) in **2** are disordered with occupancies 0.75 for Ce and 0.25 for Eu in **1**; 0.75 for La and 0.25 for Eu in **2**. In the compounds, each lanthanide is coordinated to four N and four O atoms from two $clapi^{3-}$ ligands, forming a distorted square antiprism. Two phenol oxygen atoms from the middle arms of the two heptadentate μ_2-bridging ligands connect the two Ce(Eu) atoms in **1**, and La(Eu) in **2**. The solution of the two complexes in CH_2Cl_2 exhibits red fluorescence from Eu^{3+} ions at 77 K, very weak at room temperature.

Keywords: Crystal structure; Fluorescence; Hetero-dinuclear lanthanide complexes

1. Introduction

The design and synthesis of polynuclear lanthanide(III) complexes has been of interest due to the potential applications of these compounds in different scientific areas [1–7]. Schiff-base ligands with N, O donor sets have often been used since the Schiff-base ligands may assemble coordination architectures directed by the lanthanide(III) ions [1, 8], while the lanthanide ions can promote Schiff-base condensation and can give access to complexes of otherwise inaccessible ligands [9]. Owing to the stabilization of Schiff bases by coordination with lanthanide ions, it is possible to study applications of the complexes. Complexes of Schiff base and lanthanide are extensively used as catalysts for RNA hydrolysis [10, 11], agents in cancer radiotherapy [12], contrast agents for NMR imaging [13, 14], and luminescent probes in visible and near IR domain [15, 16]. Dinuclear lanthanide Schiff-base complexes are attractive as simple models of polynuclear lanthanide complexes with potential applications in biology and medicine [17–21], chemistry, and technology [22]. Among the class of dinuclear lanthanide complexes, however, dinuclear lanthanide/N_4O_3 heptadentate Schiff base of api type $\{H_3api = $ 2-(2-hydroxyphenyl)-1,3-*bis*[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,

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3-imidazolidine} complexes have not drawn attention due to their unstability, sensitivity to moisture, and metal ion-promoted hydrolysis of the imine C=N linkages [17, 18]. Only two such compounds, namely [{Sm(api)}$_2$] and [{La(brapi)}$_2$] · 2CHCl$_3$, which are homo-dinuclear [17, 18], are structurally characterized. Herein, we report the structures and fluorescence of two new hetero-dinuclear lanthanide(III)/Schiff-base complexes [{Ln$_{1.5}$Eu$_{0.5}$(clapi)}$_2$] · 2CH$_3$CN {Ln = La, Ce; H$_3$clapi = 2-(5-chloride-2-hydroxyphenyl)-1,3-*bis*[4-(5-chloride-2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine}.

2. Experimental

2.1. *Materials and instruments*

All chemicals are of reagent grade. Infrared spectra were recorded on a Nicolet 170SX RT-IR spectrophotometer and elemental analysis C, H, and N) was performed on a Perkin–Elmer 240C analytical instrument, while Eu, Ce, and La were performed using an ICPS-7500 model inductively coupled plasma emission spectrometer (ICP-ES) with all samples dissolved in dilute hydrochloric acid. Fluorescence spectra for solutions of the two complexes in CH$_2$Cl$_2$ were obtained on an Aminco Bowman Series 2 luminescence spectrometer with a 10 nm bandwidth on both excitation and emission using an Nd : YAG laser.

2.2. *X-ray crystal structure determination*

Crystallographic data were collected at room temperature on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation. A hemisphere of data was collected at 10 s/frame and integrated with the manufacturer's SMART and SAINT software, respectively. The diffraction decay was negligible because the single crystal was enwrapped in cyanoacrylate (super glue) adhesive during data collection process which was finished within 6 h, though data collection was done at room temperature. Cell constants were refined with SAINT. Absorption corrections were applied using Sheldrick's SADABS [23] program and the structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL Version 5.03 [24]. The Ce and Eu atoms were disordered in **1** and their occupancies were refined to 0.75 for Ce and 0.25 for Eu. The La and Eu atoms were also found disordered in **2** with occupancies of 0.75 for La and 0.25 for Eu. Relevant details of the structure determination are presented in table 1 and selected bond distances and angles in table 2. Further details of the crystal structures can be obtained on quoting the depository numbers CCDC-155112 and CCDC-684148.

2.3. *Preparation of [{Ln$_{1.5}$Eu$_{0.5}$(clapi)}$_2$] · 2CH$_3$CN (Ln = La, Ce)*

To a solution of 0.4695 g (3.0 mmol) 5-chloro-salicylaldehyde in methanol (100 mL) was added 1.0 mmol Ln(NO$_3$)$_3$·6H$_2$O (Ln = La or Ce) and 1.0 mmol Eu(NO$_3$)$_3$·6H$_2$O in methanol (20 mL) and the resulting solution refluxed for 1 h. Excess triethylenetetramine (0.5840 g, 4.0 mmol) was added to the solution and the solution was allowed to reflux for

Table 1. Crystallographic data for **1** and **2**

Complexes	**1**	**2**
Color	Red	Pale yellow
Empirical formula	$C_{58}H_{54}Ce_{1.5}Cl_6Eu_{0.5}N_{10}O_6$	$C_{58}H_{54}Cl_6Eu_{0.5}La_{1.5}N_{10}O_6$
Formula weight	1485.97	1484.16
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)		
a	10.6738(2)	10.6159(16)
b	11.4924(2)	11.5309(19)
c	13.91350(10)	13.961(4)
α	109.5540(10)	109.545(18)
β	97.9510(10)	97.910(16)
γ	105.9490(10)	106.156(14)
V (Å^3)	1495.61(4)	1495.9(5)
Z	1	1
D_{Calc} (Mg m^{-3})	1.650	1.648
$F(000)$	741	739
Crystal size	0.30 × 0.24 × 0.14 mm	0.31 × 0.22 × 0.14 mm
Theta range for data collection (°)	1.61–28.32	2.00–25.01
Reflections collected/unique	10,913/7136 [R(int) = 0.0636]	6045/5126 [R(int) = 0.0577]
Max. and min. transmission	0.7697 and 0.5890	0.778 and 0.574
Data/restraints/parameters	7136/0/371	5126/0/371
Goodness-of-fit on F^2	0.907	1.007
Independent reflections	7136 [R(int) = 0.0636]	5126 [(R(int) = 0.0577]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0530$, $wR_2 = 0.1134$	$R_1 = 0.0919$, $wR_2 = 0.2129$
R indices (all data)	$R_1 = 0.0717$, $wR_2 = 0.1193$	$R_1 = 0.1258$, $wR_2 = 0.2463$
Extinction coefficient	0.0061(5)	0.063(4)
Completeness to θ	95.7%	97.0%
Largest diff. peak and hole (e Å^{-3})	2.125 and −2.203	2.421 and −2.014

2 days. The initial pale yellow solution turned slowly red (Ln=Ce) or yellow (Ln=La) on addition of triethylenetetramine. Red (Ln=Ce) or pale yellow (Ln=La) precipitates were collected (30–40% yield) and dried in vacuum. Single crystals of **1** and **2**, suitable for X-ray diffraction, were obtained by recrystallization in 1 : 1 CH_3CN/CH_2Cl_2. Anal. Calcd for $C_{58}H_{54}N_{10}Cl_6Ce_{1.5}Eu_{0.5}$ (**1**) (%): C, 46.88; H, 3.66; N, 9.43; Ce, 14.14; Eu, 5.11. Found: C, 47.1; H, 3.7; N, 9.5; Ce, 14.2; Eu, 5.0. Anal. Calcd for $C_{58}H_{54}N_{10}Cl_6La_{1.5}Eu_{0.5}$ (**2**) (%): C, 46.94; H, 3.67; N, 9.44; La, 14.04; Eu, 5.12. Found: C, 47.0; H, 3.7; N, 9.3; La, 14.1; Eu, 5.2.

3. Results and discussion

3.1. *Preparation of the complexes*

Preparation and molecular structure of H_3clapi have been reported and the reaction of H_3clapi with Ln^{3+} produced a few homo-dinuclear complexes of the general formula [Ln(clapi)]$_2$ ($Ln^{3+} = La^{3+}$, Pr^{3+}, Nd^{3+}, Yb^{3+}, and Gd^{3+}) through non-template reaction [17]. In our experiment, interaction of an excess of triethylenetetramine and salicylaldehyde in the presence of Eu^{3+}/Ln^{3+} ($Ln^{3+} = La^{3+}$ or Ce^{3+}) ions in methanol gives hetero-dinuclear complexes [{$Ln_{1.5}Eu_{0.5}$(clapi)}$_2$] (Ln = La, Ce), where Ln^{3+} is

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Selected bond lengths and angles for **1**			
Ce(1)–O(3)	2.311(4)	Ce(1)–Eu(1)#1	4.0040(5)
Ce(1)–O(2)	2.426(3)	O(1)–Eu(1)#1	2.325(4)
Ce(1)–N(1)#1	2.557(4)	O(2)–Ce(1)#1	2.428(3)
Ce(1)–N(4)	2.567(5)	N(2)–Eu(1)#1	2.840(4)
Ce(1)–N(3)	2.835(4)		
O(3)–Ce(1)–O(1)#1	129.40(13)	O(2)#1–Ce(1)–N(2)#1	70.24(11)
O(3)–Ce(1)–O(2)	82.95(12)	N(1)#1–Ce(1)–N(2)#1	64.45(13)
O(1)#1–Ce(1)–O(2)	145.37(11)	N(4)–Ce(1)–N(2)#1	147.22(13)
O(3)–Ce(1)–O(2)#1	143.71(12)	N(3)–Ce(1)–N(2)#1	146.45(12)
O(1)#1–Ce(1)–O(2)#1	84.48(12)	N(4)–Ce(1)–N(3)	64.29(13)
O(2)–Ce(1)–O(2)#1	68.83(13)	O(3)–Ce(1)–N(2)#1	83.98(13)
O(3)–Ce(1)–N(1)#1	73.68(14)	O(1)#1–Ce(1)–N(2)#1	110.14(13)
O(1)#1–Ce(1)–N(1)#1	70.37(13)	O(2)–Ce(1)–N(2)#1	81.89(11)
O(2)–Ce(1)–N(1)#1	140.36(12)	N(1)#1–Ce(1)–N(3)	148.25(13)
O(2)#1–Ce(1)–N(1)#1	114.41(13)	O(2)#1–Ce(1)–N(4)	141.54(12)
O(3)–Ce(1)–N(4)	70.27(14)	N(1)#1–Ce(1)–N(4)	88.43(14)
O(1)#1–Ce(1)–N(4)	74.31(14)	O(3)–Ce(1)–N(3)	108.83(13)
O(2)–Ce(1)–N(4)	113.47(13)	O(1)#1–Ce(1)–N(3)	86.01(12)
O(2)#1–Ce(1)–N(3)	82.86(11)	O(2)–Ce(1)–N(3)	69.62(11)
Selected bond lengths and angles for **2**			
Eu(1)–O(3)	2.333(10)	O(1)–La(1)#1	2.358(10)
Eu(1)–O(1)#1	2.358(10)	O(1)–Eu(1)#1	2.358(10)
Eu(1)–O(2)	2.436(9)	O(2)–La(1)#1	2.445(8)
Eu(1)–O(2)#1	2.445(8)	O(2)–Eu(1)#1	2.445(8)
Eu(1)–N(1)#1	2.583(10)	N(1)–La(1)#1	2.583(10)
Eu(1)–N(4)	2.583(12)	N(1)–Eu(1)#1	2.583(10)
Eu(1)–N(2)#1	2.863(11)	N(2)–La(1)#1	2.863(11)
Eu(1)–N(3)	2.866(10)	N(2)–Eu(1)#1	2.863(11)
O(3)–Eu(1)–O(1)#1	129.0(3)	O(2)#1–Eu(1)–N(1)#1	114.3(3)
O(3)–Eu(1)–O(2)	83.0(3)	O(3)–Eu(1)–N(4)	69.9(3)
O(1)#1–Eu(1)–O(2)	145.8(3)	O(1)#1–Eu(1)–N(4)	75.1(3)
O(3)–Eu(1)–O(2)#1	143.8(3)	O(2)–Eu(1)–N(4)	112.6(3)
O(1)#1–Eu(1)–O(2)#1	84.8(3)	O(2)#1–Eu(1)–N(4)	141.3(3)
O(2)–Eu(1)–O(2)#1	68.6(3)	N(1)#1–Eu(1)–N(4)	89.7(4)
O(3)–Eu(1)–N(1)#1	73.7(3)	O(3)–Eu(1)–N(2)#1	84.5(3)

Note: Symmetry transformations used to generate equivalent atoms for (1): #1 $-x+1$, $-y-1$, $-z+1$; (**2**): #1 $-x$, $-y$, $-z$.

a template to promote Schiff-base condensation giving clapi^{3-} and coordinating with it [9, 18].

3.2. *Infrared spectra*

In the IR spectra of **1** and **2**, the strong band at 1626 (**1**) and 1632 cm^{-1} (**2**) is attributed to the imine C=N stretch, indicating formation of the ligand during the synthesis. The imine C=N stretching vibration band shifts from 1634 cm^{-1} in the free ligand prepared according to the method reported [17] to 1626 and 1632 cm^{-1} in **1** and **2**, respectively, due to coordination. The C–O stretch at 1279 cm^{-1} in the free ligand shifts to 1303 and 1323 cm^{-1} in **1** and **2**, respectively, because of deprotonation of the phenolic hydroxyl and subsequent coordination to lanthanide, consistent with the lack of a broad peak due to O–H stretching in the range of 3300–2100 cm^{-1}, confirming deprotonation of all phenolic functions [25].

3.3. *Molecular structures of the complexes*

X-ray crystallographic analysis reveals that **1** and **2** are isostructural, so **1** is selected as the representative for discussion. As shown in figure 1, Ce and Eu atoms are disordered in **1** with occupancies of 0.75 and 0.25, respectively. The Ce(Eu) is coordinated to four N and O atoms of the ligand, with Ce(Eu)–O distances in the range of 2.311(4)–2.428(3) Å [av. Ce(Eu)–O = 2.373 Å], and Ce(Eu)–N distances from 2.557(4) to 2.840(4) Å [av. Ce(Eu)–N = 2.700 Å], forming a distorted square antiprism (figure 2). The O–Ce(Eu)–O

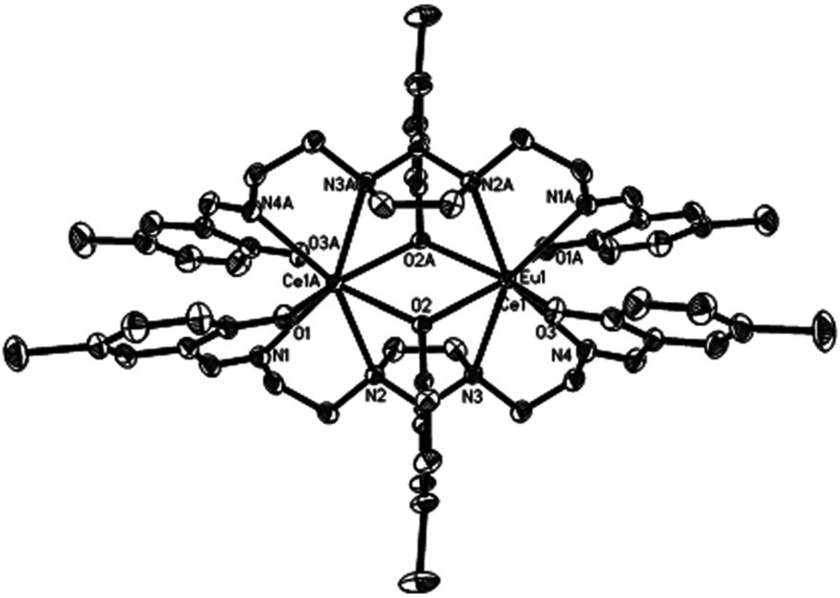

Figure 1. ORTEP view of **1** showing the atom-labeling scheme with 30% probability ellipsoids (CH_3CN was omitted for clarity).

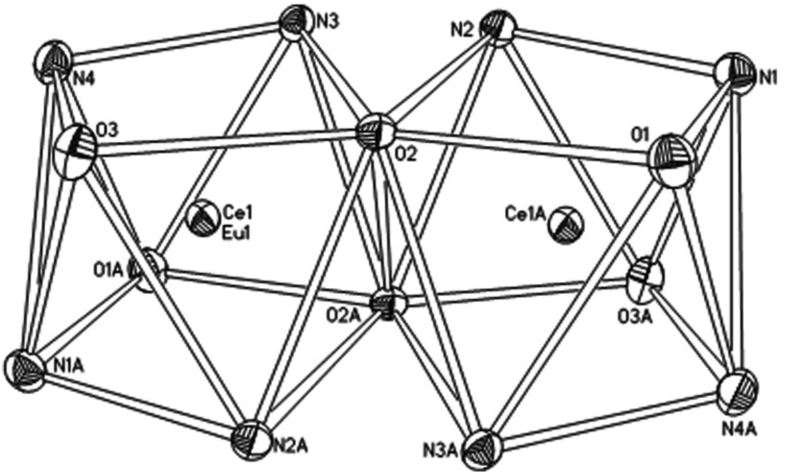

Figure 2. Coordination polyhedron around the two Ce(Eu) ions in **1**.

bond angles are in the range of 68.83(13)–143.71(12)°, O–Ce(Eu)–N bond angles in the range of 69.62(11)–141.54(12)°, N–Ce(Eu)–N bond angles in the range of 64.29(13)–148.25(13)°. Of the four oxygens connected to Ce(Eu), two are from terminal phenols and the other two, as μ_2-bridging, are from the middle arms of the two heptadentate ligands. Of the four nitrogens, two are from imidazolidine, while the other two are from imines. The average Ce(Eu)–N (imidazolidine) bond length (2.838 Å) is significantly longer than that of Ce(Eu)–N (imine) (2.562 Å); the average Ce(Eu)–O (the middle arms of the two heptadentate ligands) bond lengths (2.427 Å) are longer than that of Ce(Eu)–O (terminal phenols) (2.318 Å). The two coordination polyhedra of $Ce(Eu)^{3+}$ edge-share through O(2)···O(2a) (2.764 Å in **1**) (figure 2). The intramolecular distances of Ce(Eu)(1)–Ce(Eu)(1a) are 4.004 Å. The four nitrogens of the ligand are coplanar within maximum deviation of 0.013 Å and the two terminal phenolate rings are inclined by ca. 17.4°, smaller than 25° reported [18].

3.4. *Fluorescence of the title complexes*

Fluorescence spectra are studied for the complexes in CH_2Cl_2 solution at room temperature and 77 K. Figure 3 shows the excitation spectra and emission spectra of **1** and **2** at room temperature. Broad peaks at 390 nm in the excitation spectra of **1** and **2** can be assigned to the $\pi \rightarrow \pi^*$ transition of the ligand, but the band at 320 nm in the excitation spectrum of **1** is mainly ascribed to the spin-allowed transition from 4f to 5d of Ce^{3+} [26]. In the emission spectra of **1** and **2**, the strong and broad band in the range

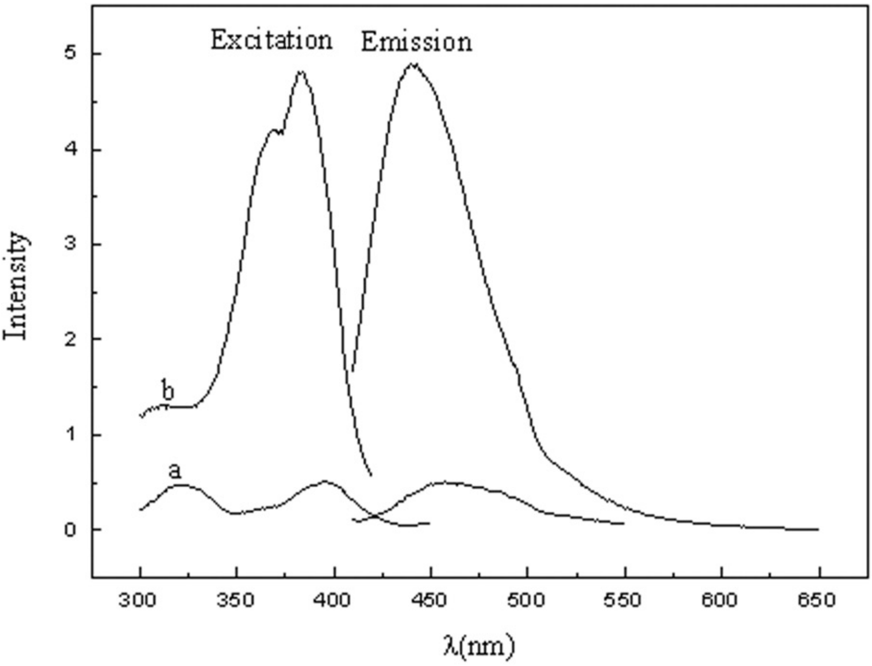

Figure 3. The excitation and emission spectra of **1** and **2** at room temperature. (a) The excitation and emission spectra of **1** (1.8×10^{-5} mol L^{-1}) in CH_2Cl_2 ($\lambda_{em} = 460$ nm, $\lambda_{exc} = 396$ nm); (b) the excitation and emission spectra of **2** (1.8×10^{-5} mol L^{-1}) in CH_2Cl_2 ($\lambda_{em} = 440$ nm, $\lambda_{exc} = 394$ nm).

Table 3. Fluorescence spectral data of **1** and **2** assigned for Eu^{3+}.

1		**2**	
λ(nm)	Assignment	λ(nm)	Assignment
580	$^5D_0 \rightarrow {}^7F_0$	580	$^5D_0 \rightarrow {}^7F_0$
590	$^5D_0 \rightarrow {}^7F_1$	592	$^5D_0 \rightarrow {}^7F_1$
596	$^5D_0 \rightarrow {}^7F_1$	594	$^5D_0 \rightarrow {}^7F_1$
613	$^5D_0 \rightarrow {}^7F_2$	612	$^5D_0 \rightarrow {}^7F_2$
618	$^5D_0 \rightarrow {}^7F_2$	617	$^5D_0 \rightarrow {}^7F_2$
628	$^5D_0 \rightarrow {}^7F_2$	628	$^5D_0 \rightarrow {}^7F_2$
652	$^5D_0 \rightarrow {}^7F_3$	650	$^5D_0 \rightarrow {}^7F_3$
691	$^5D_0 \rightarrow {}^7F_4$	692	$^5D_0 \rightarrow {}^7F_4$
695	$^5D_0 \rightarrow {}^7F_4$	694	$^5D_0 \rightarrow {}^7F_4$
703	$^5D_0 \rightarrow {}^7F_4$	704	$^5D_0 \rightarrow {}^7F_4$

of 430–470 nm ($\lambda_{\max} = 450$ nm or 460 nm) can be attributed to the $\pi \rightarrow \pi^*$ transition of the ligand. There is no red fluorescence of Eu^{3+} in the fluorescence spectra of **1** and **2** at room temperature.

In the excitation spectra of **1** and **2** irradiated by 628 nm light at 77 K (Supplementary Material), a band at 360 nm is very strong and broad, appearing instead of the band at 390 nm which disappeared (perhaps covered by the band at 360 nm), indicating formation of **1** and **2**. Emission spectra of **1** and **2** are typically for Eu^{3+} ($^5D_0 \rightarrow {}^7F_j$) emission which are very strong at 77 K even though they cannot be observed at room temperature, indicating efficient energy transfer from the ligand to Eu^{3+} at low temperature. Emission spectra of **1** and **2** have one peak at 580 nm for the forbidden $^5D_0 \rightarrow {}^7F_0$ transition, two peaks at about 590 nm for $^5D_0 \rightarrow {}^7F_1$, three peaks at 612 nm, 618 and 628 nm for $^5D_0 \rightarrow {}^7F_2$, 1 weak and broad peak at 650 nm for $^5D_0 \rightarrow {}^7F_3$ and more peaks around 684 and 703 nm for $^5D_0 \rightarrow {}^7F_4$ (see table 3). Only one peak for the $^5D_0 \rightarrow {}^7F_0$ forbidden transition is observed in **1** and **2**, indicating that there is only one site of Eu^{3+} in the two complexes. In the 32 point groups, there are only C_1, C*s*, C*n*, and C*nv* in which $^5D_0 \rightarrow {}^7F_0$ transition can be observed. In **1** and **2** the local symmetry of Eu^{3+} ions is C_1 after it is excited [27]. The electric dipole transition $^5D_0 \rightarrow {}^7F_2$ is more intense than the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ reflecting the low site symmetry of Eu^{3+}.

4. Conclusions

Both **1** and **2** in CH_2Cl_2 at 77 K exhibit typical Eu^{3+} red fluorescence that cannot be observed at room temperature. The fluorescence enhancement of Eu^{3+} ions at 77 K in **1** and **2** indicates efficient energy transfer from the Schiff base to Eu^{3+}.

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References

[1] P.A. Vigato, S. Tamburini. *Coord. Chem. Rev.*, **248**, 1717 (2004).
[2] V. Alexander. *Chem. Res.*, **95**, 273 (1995).
[3] C. Benelli, D. Gatteschi. *Chem. Rev.*, **102**, 2369 (2002).
[4] A. Dossing. *Eur. J. Inorg. Chem.*, **8**, 1425 (2005).
[5] J.-C.G. Bünzli, C. Piguet. *Chem. Rev.*, **102**, 1897 (2005).
[6] N. Sabbatiui, M. Guardagli, J.M. Lehn. *Coord. Chem. Rev.*, **123**, 201 (1993).
[7] D. Parker, R.S. Dickins, H. Puschmann, C. Crossland, J.A.K. Howard. *Chem. Rev.*, **102**, 1977 (2002).
[8] W. Radecka-Paryzek, V. Patroniak, J. Lisowski. *Coord. Chem. Rev.*, **249**, 2156 (2005).
[9] M. Tsiouria, N. Hadjiliadis, T. Arslan, B.M. Kariuki, J.C. Plakatouras. *Inorg. Chem. Commun.*, **9**, 429 (2006).
[10] W. Radecka-Paryzek, V. Patroniak, J. Lisowski. *Coord. Chem. Rev.*, **249**, 2156 (2005).
[11] A. Roigk, R. Hettich, H.-J. Schneider. *Inorg. Chem.*, **37**, 751 (1998).
[12] G.K. Denardo, G.R. Mirik, LA. Kroger, R.T.O. Donnel, C.F. Meares, S.L. Denardo. *J. Nucl. Med.*, **37**, 451 (1996).
[13] J.A. Peters, J. Huskens, D.J. Raber. *Prog. Magn. Reson. Spectrosc.*, **28**, 283 (1996).
[14] P. Caravan, J.J. Ellison, T.J. McMurry, R.B. Lauffer. *Chem. Rev.*, **99**, 2293 (1999).
[15] V.W.-W. Yam, K.K.-W. Lo. *Coord. Chem. Rev.*, **184**, 157 (1999).
[16] D. Imbert, S. Comby, A.-S. Chauvin, J.-C. Bünzli. *Chem. Commun.*, 1432 (2005).
[17] L.W. Yang, S. Liu, E. Wong, S.J. Rettig, C. Orvig. *Inorg. Chem.*, **34**, 2164 (1995).
[18] R.C. Howell, K.V.N. Spence, I.A. Kahwa, D.J. Williams. *J. Chem. Soc., Dalton Trans.*, 2727 (1998).
[19] C. Liu, M. Wang, T. Zhang, H. Sun. *Coord. Chem. Rev.*, **248**, 147 (2004).
[20] M.K. Thomson, D.M.J. Doble, L.S. Tso, S. Barra, M. Botta, S. Aime, K.N. Raymond. *Inorg. Chem.*, **43**, 8577 (2004).
[21] J.-C.G. Bünzli, C. Piguet. *Chem. Rev.*, **102**, 1897 (2002).
[22] P.M.T. Piggot, L.A. Hall, A.J.P. White, D.J. Williams. *Inorg. Chem.*, **42**, 8344 (2003).
[23] G.M. Sheldrick. *SADABS*, University of Gottingen, Germany (1996).
[24] G.M. Sheldrick. *SHELXTL V5.1, Software Reference Manual*, Bruker AXS, Inc., Madison, WI (1997).
[25] S. Salehzadeh, S.M. Nouri, H. Keypour, M. Bagherzadeh. *Polyhedron*, **24**, 1478 (2005).
[26] H.P. You, G.Y. Hong. *Chin. Chem. Lett.*, **9**, 877 (1998).
[27] C.H. Huang. *Coordination Chemistry of Rare Earth*, Science Publishing Co., Science Press, Peking (1997).