PERGAMON

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 22 (2003) 323–330

POLYHEDRON

www.elsevier.com/locate/poly

Structure and photophysical properties of europium complexes of succinamic acid and 1,10-phenanthroline

Xiang-Jun Zheng [a], Lin-Pei Jin [a,*], Zhe-Ming Wang [b], Chun-Hua Yan [b], Shao-Zhe Lu [c], Qi Li [a]

[a] *Department of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China*

[b] *State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China*

[c] *Laboratory of Excited States Processes, Chinese Academy of Sciences, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130021, People's Republic of China*

Received 30 July 2002; accepted 21 October 2002

Abstract

Two binuclear europium complexes $[Eu_2(SA)_6(phen)_2]\cdot 6H_2O$ (**1**) and $[Eu_2(SA)_4(phen)_2(H_2O)_4](ClO_4)_3$ $(phenH)\cdot H_2O$ (**2**) (where SA = succinamate, phen = 1,10-phenanthroline) have been synthesized and characterized by X-ray single crystal diffraction. For **1**, the unit cell contains two crystallographically independent $Eu(SA)_3(phen)$ species in which the Eu^{3+} ions have two different coordination environments. Two types of binuclear molecule are arranged in different orientations in the crystal. The $^7F_0 \rightarrow {}^5D_0$ excitation peaks at 580.16 and 580.46 nm at 77 K and the Stark components of $^5D_0 \rightarrow {}^7F_J$ transitions, especially $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ emission lines, show that complex **1** has two Eu(III) ion sites, which is in good agreement with the results of the structure determination. In complex **2**, four water molecules take the place of two bidentate chelating SA anions in the inner coordination sphere of **1**. Outside the coordination sphere, the protonated phen molecule forms a hydrogen bond with a tridentate-coordinated carboxyl group and has a π–π stacking interaction with the coordinated phen molecule.

Keywords: Europium complex; X-ray crystallography; Photophysical property; 1,10-Phenanthroline; Succinamic acid

1. Introduction

Lanthanide coordination compounds with carboxylic acids, amino acids and polyamino polycarboxylic acids have been extensively studied due to the various coordination modes of the carboxyl group which leads to complex structures [1–5]. Generally speaking, for the lanthanide complexes of monocarboxylic acid, the solvent water molecules are usually involved in coordination with the lanthanide ion because the coordination number of the lanthanide ion is relatively large (CN = 8–12) [6], and thus the europium complexes show weak luminescence since the high-frequency O–H vibrations will deactivate the metal-centered excited states [7]. Phen is usually selected as the second ligand to compete with water in coordination for its chelating effect, and as a consequence, increase the fluorescence intensity of the lanthanide complexes due to its 'antenna' effect [8–10]. Owing to the beneficial luminescence characteristics such as narrow emission lines in the visible range, intensive fluorescence and long-lived excited states, europium complexes are more widely investigated. For the europium (III) ion, its lowest emission level $^5D_0$ is non-degenerate, so there should be only one emission line for the $^5D_0 \rightarrow {}^7F_0$ transition, which can be used to probe the local structure in the crystal including determination of local symmetry and the number of different coordination sites [11–14]. For most lanthanide complexes with carboxylic acid, binuclear molecules arranged periodically in the crystal are common, but to our knowledge, relatively little work has been done on lanthanide complexes in which two binuclear

---

* Corresponding author. Tel.: +86-10-6220-5522; fax: +86-10-6220-0567

E-mail address: lpjin@bnu.edu.cn (L.-P. Jin).

0277-5387/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0277-5387(02)01361-X

molecules with the same coordination number and ligands orientate differently in the crystal. In this paper, the structure and photophysical properties of an unusual europium complex **1** possessing two types of chemical environments for the Eu^{3+} ions in the crystal as well as those of another europium complex **2** resulting from different reaction conditions are presented and discussed.

2. Experimental

All reagents used were of analytical grade and used without further purification. The stock solution of $Eu(ClO_4)_3$ was obtained by dissolving Eu_2O_3 (99.99%) in concentrated $HClO_4$ and diluted with distilled water to 0.57 M. Succinamic acid was purchased from Acros Co. Ltd., and phen·H_2O from Beijing Xizhong Chemical Factory.

2.1. Preparation of complexes

2.1.1. $[Eu_2(SA)_6(phen)_2]\cdot 6H_2O$

Succinamic acid (0.351 g, 3 mmol) and phen·H_2O (0.198 g, 1 mmol) were dissolved in 8 ml of ethanol (95%) with stirring at 75 °C. Eu_2O_3 (0.176 g, 0.5 mmol) was added to the solution, the mixture was heated under reflux for 6 h and a precipitate formed. The filtrate was allowed to stand at room temperature (r.t.) for 10 days to obtain colorless crystals in 38% yield. *Anal.* Calc. for $C_{48}H_{64}Eu_2N_{10}O_{24}$: C, 39.24; H, 4.39; N, 9.53. Found: C, 39.61; H, 4.05; N, 9.38%.

2.1.2. $[Eu_2(SA)_4(phen)_2(H_2O)_4]$-$(ClO_4)_3(phenH)(H_2O)$

Succinamic acid (0.2 g, 1.7 mmol) was added to 6 ml of ethanol (95%), to which 1 ml aqueous solution of $Eu(ClO_4)_3$ (0.57 M) was added. The mixture was heated at 50 °C with stirring and then 0.3 ml NaOH aqueous solution (0.65 M) was added. After 0.5 h, 4 ml of ethanolic solution of phen (0.226 g, 1.14 mmol) was added dropwise. The reaction temperature was controlled at about 60 °C for 12 h. The mixture was kept at r.t. for 2 months and colorless crystals were obtained in 60% yield. *Anal.* Calc. for $C_{52}H_{59}Cl_3Eu_2N_{10}O_{29}$: C, 36.64; H, 3.84; N, 8.22. Found: C, 36.85; H, 3.51; N, 7.95%.

2.2. X-ray crystallographic analysis

The diffraction data of the complexes **1** and **2** were collected at 293 K with a Nonius Kappa CCD area detector and a Bruker Smart CCD area detector, respectively, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 programs [15]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. The rather high wR_2 value for the structure of **2** is due to the high thermal motion of the perchlorate anion and free phen molecule.

2.3. Measurement of the high-resolution luminescence spectra

The excitation light source was a YAG: Nd laser which emits at 1.064 μm, and the excitation wavelength was 355 nm. The sample was placed in a Dewar and cooled with liquid nitrogen. The fluorescence was collected at right angles through a Spex 1403 monochromator with a photomultiplier tube, then averaged by Boxcar integrator and finally data were transferred to a computer.

3. Results and discussion

3.1. X-ray crystallography

A summary of crystallographic data for **1** and **2** is given in Table 1, and selected bond lengths are shown in Table 2.

Table 1
Summary of crystallographic data for **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{48}H_{64}Eu_2N_{10}O_{24}$	$C_{52}H_{59}Cl_3Eu_2N_{10}O_{29}$
M	1469.01	1698.36
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.2881(3)	10.950(4)
b (Å)	13.6425(4)	12.718(4)
c (Å)	21.1517(7)	13.766(4)
α (°)	74.281(2)	62.544(5)
β (°)	79.525(1)	76.584(5)
γ (°)	72.036(1)	88.290(5)
V (Å^3)	2965.4(2)	1648.0(9)
D_{calc} (g cm^{-3})	1.645	1.711
T (K)	293(2)	293(2)
Z	2	1
μ (mm^{-1})	2.183	2.100
Reflections collected:		
Total, independent, R_{int}	58 547, 13 571, 0.0915	6891, 5790, 0.0248
Final R_1, wR_2: $[I > 2\sigma(I)]$	0.0428, 0.0776	0.0389, 0.1080
(all data)	0.0882, 0.0889	0.0452, 0.1116

Table 2
Selected bond lengths (Å) in **1** and **2**

1				2	
Eu(1)–O(1)	2.541(3)	Eu(2)–O(10)	2.508(3)	Eu(1)–O(1)	2.335(4)
Eu(1)–O(2)	2.474(3)	Eu(2)–O(10)#2	2.398(3)	Eu(1)–O(2)#3	2.366(4)
Eu(1)–O(4)	2.549(3)	Eu(2)–O(11)	2.512(3)	Eu(1)–O(4)	2.362(4)
Eu(1)–O(4)#1	2.372(3)	Eu(2)–O(13)	2.478(3)	Eu(1)–O(4)#3	2.663(4)
Eu(1)–O(5)	2.519(3)	Eu(2)–O(14)	2.478(3)	Eu(1)–O(5)#3	2.446(4)
Eu(1)–O(7)	2.376(3)	Eu(2)–O(16)	2.408(3)	Eu(1)–O(7)	2.464(5)
Eu(1)–O(8)#1	2.345(3)	Eu(2)–O(17)#2	2.354(3)	Eu(1)–O(8)	2.443(5)
Eu(1)–N(1)	2.624(4)	Eu(2)–N(6)	2.556(4)	Eu(1)–N(1)	2.613(5)
Eu(1)–N(2)	2.591(5)	Eu(2)–N(7)	2.610(4)	Eu(1)–N(2)	2.608(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y$, $-z$; #2 $-x+2$, $-y-1$, $-z+1$; #3 $-x+1$, $-y+1$, $-z+1$.

3.2. Complex 1

Interestingly, there are two crystallographically different Eu$_2$(SA)$_6$(phen)$_2$ species in the unit cell, and thus **1** contains two types of binuclear molecule, a property which is rarely reported in the literature. The dimetallic units are both located on inversion centers and the molecular structures are shown in Fig. 1(a) and (b). Of the carboxylate groups in (a) and (b), two are bidentate bridging, two tridentate chelating-bridging and the remaining two bidentate chelating. The central Eu1 in (a) and Eu2 in (b) are both nine-folded coordinated, but what is worth noting is the difference in the Eu–O and Eu–N lengths and the corresponding bond angles and thus the coordination polyhedrons of the central Eu(III) ions in the two binuclear molecules. The polyhedron for the Eu1 ion in (a) is a tricapped trigonal prism. The three cap positions are occupied by O2, N1 and O4 atoms and the other coordinated atoms constitute the six apical positions of the trigonal prism. Considering that the distance between the two chelating oxygen atoms O2–O1 (2.198 Å) is much shorter than those between O2 and O(4A) (2.992 Å), O(8A) (2.902 Å), N2(2.956 Å), and so is the same case for another cap O4, it can be concluded that Eu1 is in a distorted tricapped trigonal prism. However, the coordination polyhedron for Eu2 in Fig. 1(b) is a monocapped square-antiprism, in which the cap position is occupied by one of the chelating oxygen atoms O13. The four apical positions of the upper square are occupied by O14, N6, O16 and O(10A) which deviate from the plane by 0.1128, 0.1221, 0.1392 and 0.1298 Å, respectively, and those of the lower square by O(17A), N7, O11 and O10, which have good coplanarity. The dihedral angle between the two squares is 4.7°. The angles between adjacent edges on the upper plane are near 90° (87.5°, 87.4°, 84.8° and 96.9°), while those for the lower plane are 94.7°, 84.4°, 77.5° and 103°. Therefore, the coordination polyhedron of Eu2 is a distorted monocapped square-antiprism. Fig. 2 illustrates the two types of binuclear Eu–Eu molecules in the crystal, the Eu1–Eu(1A) binuclear molecule alternates with the Eu2–Eu(2A) binuclear molecule in column along the *c* axis, showing that their coordinated phen runs parallel to one another in the crystal.

Since there are six uncoordinated water molecules for each binuclear structure and the ligand SA has an amido

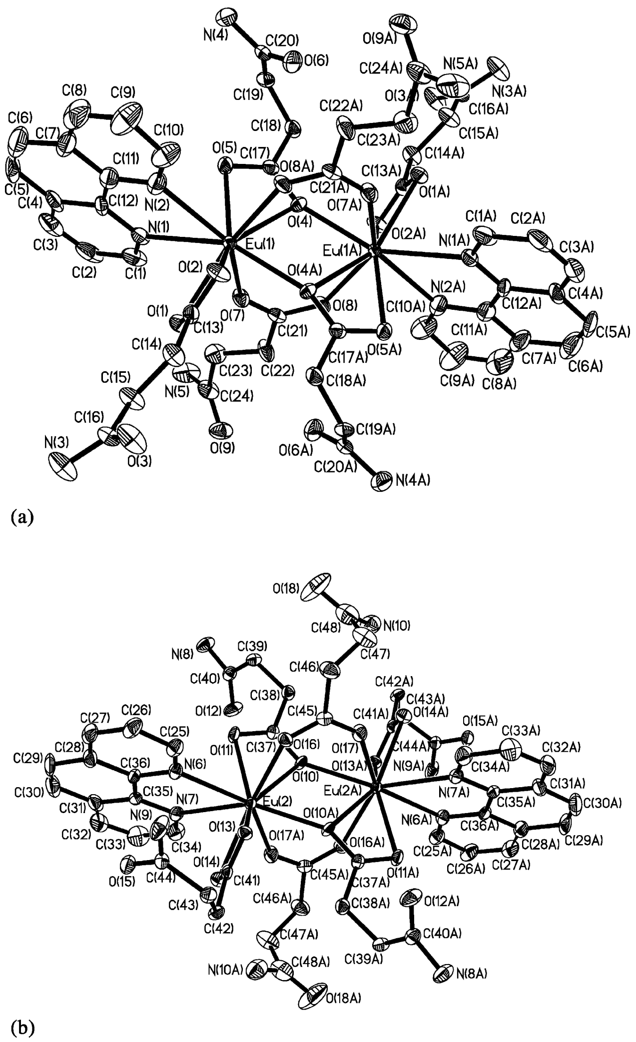

Fig. 1. (a) and (b) ORTEP diagram with partial atom numbering scheme of **1** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

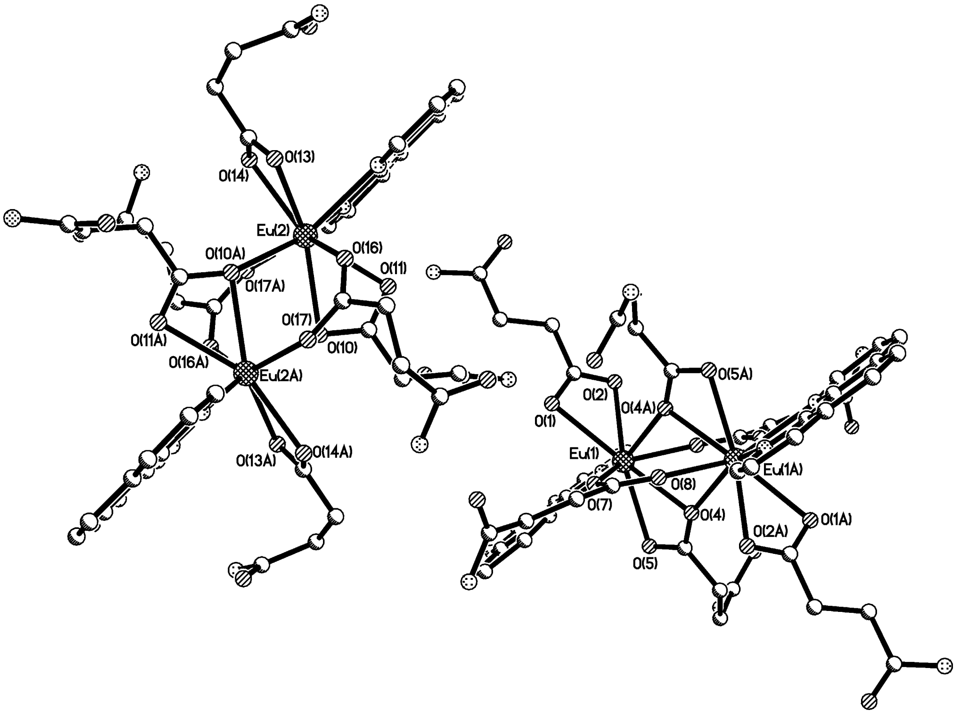

Fig. 2. Perspective view of **1** showing the different orientations of ligands in the different binuclear structures.

group, hydrogen bonds of the type N–H···O and O–H···O (Table 3) connect the binuclear complexes to form a network.

3.3. Complex 2

The pH value of the reaction system for complex **2** was low. Although the mole ratio of Eu^{3+} and succinamic acid used was the same as that for **1**, deprotonation of the carboxyl groups of succinamic acid in **2** is difficult to occur, while phen is liable to be protonated at lower pH, and thus it is not easy for two phen molecules to coordinate with one Eu^{3+} ion simultaneously. The Eu^{3+} ion completes its coordination sphere by binding small solvent molecules such as water because the number of available sites offered by the ligand is low. To balance the positive charge, ClO_4^- stays in the lattice as the counteranion. Fig. 3 shows the binuclear cation structure of complex **2**. Every Eu(III) ion is coordinated with two oxygen atoms from two H_2O molecules, two nitrogen atoms from one chelating phen and five oxygen atoms from four carboxylate groups which have two modes: two are bidentate bridging and the other two are tridentate chelating-bridging. Thus the Eu(III) ion in **2** is also nine-coordinated in the form of a tricapped trigonal prism. The atoms O8, N1 and O(4A) occupy the three cap positions, and the three apical positions of the upper triangle are occupied by O1, O7 and O4. Correspondingly, the lower triangle is occupied by O(5A), N2 and O(2A). The dihedral angle between the two triangles is 21.4°, and the distortion in the coordination polyhedron can be attributed to the presence of mixed and multidentate ligands around the metal ion. Two coordinated

Table 3
Hydrogen bonds in **1** (Å and °)

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(3)–H(1)···O(15)#3	0.86	2.16	3.017(5)	173.8
N(3)–H(2)···O(19)	0.86	2.01	2.839(6)	162.3
N(4)–H(4)···O(5)#4	0.86	2.15	3.008(6)	175.3
N(5)–H(5)···O(3)#5	0.86	2.07	2.865(6)	154.1
N(5)–H(6)···O(21)#6	0.86	2.05	2.901(8)	168.8
N(8)–H(7)···O(1)	0.86	2.22	3.016(5)	152.8
N(8)–H(8)···O(6)#1	0.86	2.07	2.907(6)	164.1
N(9)–H(9)···O(12)#7	0.86	2.27	3.110(6)	166.5
N(9)–H(10)···O(13)#8	0.86	2.06	2.912(5)	168.0
N(10)–H(11)···O(9)	0.86	2.15	2.995(6)	165.7
N(10)–H(12)···O(14)#2	0.86	2.32	3.017(6)	138.0
O(19)–H(53)···O(12)	0.95(2)	1.89(3)	2.795(5)	158(6)
O(19)–H(54)···O(15)#6	0.97(2)	1.82(3)	2.763(5)	164(7)
O(20)–H(55)···O(6)#1	0.96(2)	2.25(6)	2.992(8)	133(6)
O(20)–H(56)···O(18)	0.97(2)	2.06(6)	2.87(1)	139(7)
O(21)–H(57)···O(18)	1.00(2)	1.79(4)	2.716(9)	151(6)
O(21)–H(58)···O(24)	0.93(2)	2.46(6)	3.14(3)	130(6)
O(22)–H(59)···O(24)#9	1.00(2)	2.27(7)	2.93(3)	123(7)
O(22)–H(60)···O(2)	0.94(2)	2.20(7)	2.750(8)	116(6)
O(23)–H(62)···O(20)#10	0.97(2)	2.44(7)	3.11(3)	126(6)
O(24)–H(63)···O(23)#11	0.96(2)	2.17(7)	2.42(3)	93(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z$; #2 $-x+2, -y-1, -z+1$; #3 $-x+2, -y, -z+1$; #4 $-x, -y, -z$; #5 $x, y-1, z$; #6 $x-1, y, z$; #7 $x+1, y, z$; #8 $-x+3, -y-1, -z+1$; #9 $-x+2, -y, -z$; #10 $x-1, y+1, z$ #11 $x+1, y-1, z$.

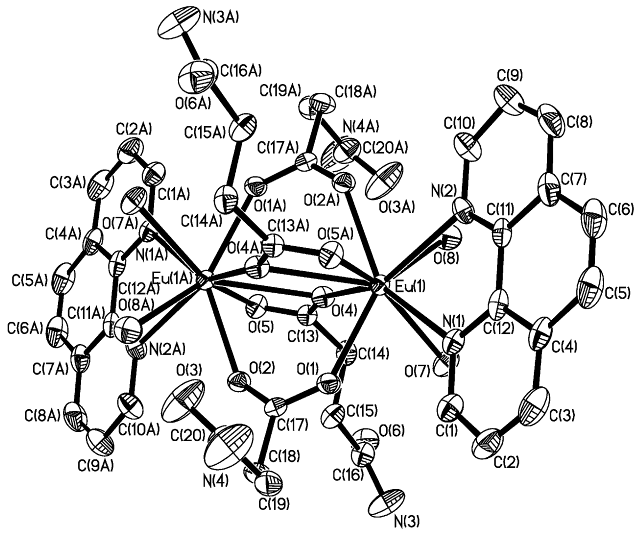

Fig. 3. ORTEP diagram with atom numbering scheme of the binuclear cation structure of **2** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

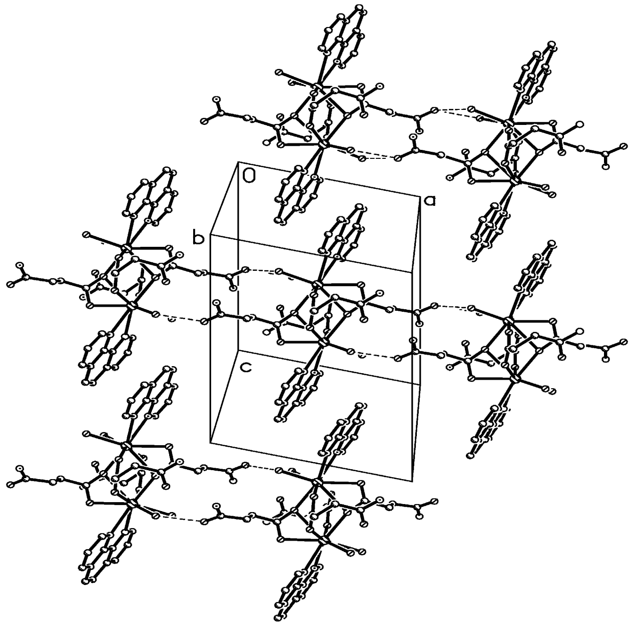

Fig. 4. Packing diagram of **2** in the direction [010]. For the interest of clarity, hydrogen atoms, ClO_4^- and uncoordinated phen are omitted.

water molecules from a binuclear molecule are simultaneously hydrogen-bonded to the carbonyl oxygen atom of an SA anion in which the carboxyl group coordinates with the Eu^{3+} ion from an adjacent binuclear molecule in the tridentate chelating-bridging mode. Thus the adjacent binuclear molecules in the direction [010] are connected together through $O_{water}-H\cdots O_{carbonyl}$ hydrogen bonds, forming a ladder-type structure as shown in Fig. 4, and the bridging carboxyl groups can be viewed as the rungs.

In the crystal there are uncoordinated phen molecules of which one of two nitrogen atoms is protonated, and the uncoordinated phen molecule connects the tridentate bridging coordinated SA through a $N-H\cdots O_{carboxyl}$ hydrogen bond. Two coordinated phen from different binuclear complexes are in alternation with an uncoordinated phen. All phen molecules, coordinated and uncoordinated, are parallel to one another with π–π stacking interactions between them. The average distance between two parallel phen molecules is 3.47 Å. Such π–π stacking interaction and

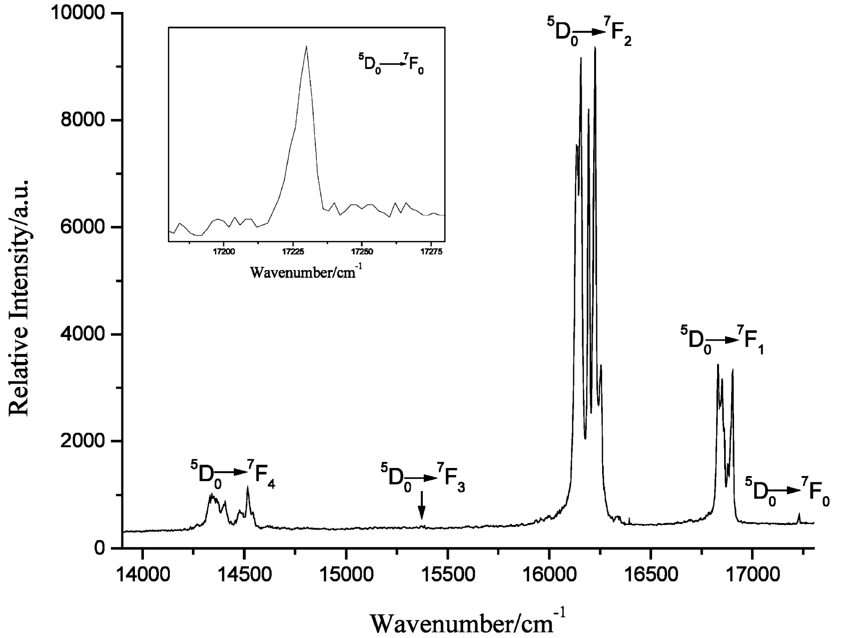

Fig. 5. Emission spectra of complex **1** corresponding to $^5D_0 \rightarrow {}^7F_J (J = 0–4)$ transitions at 77 K, $\lambda_{exc} = 355$ nm.

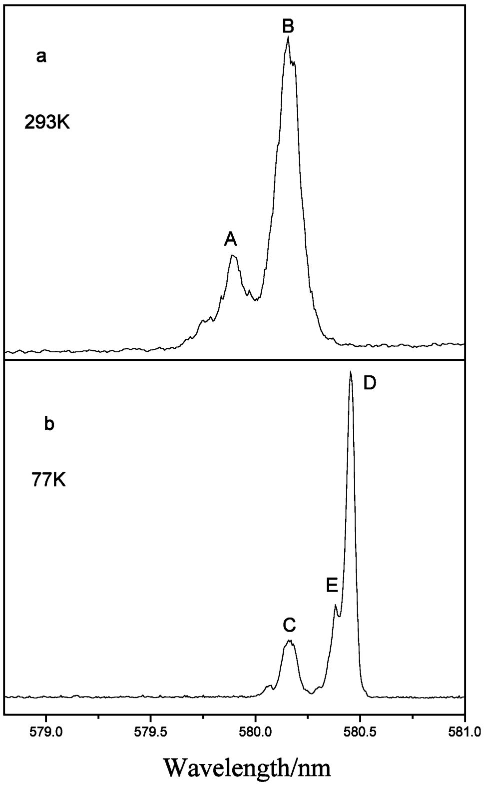

Fig. 6. Excitation spectra of complex **1** at 293 and 77 K, analyzing wavenumber: 16141 cm^{-1}.

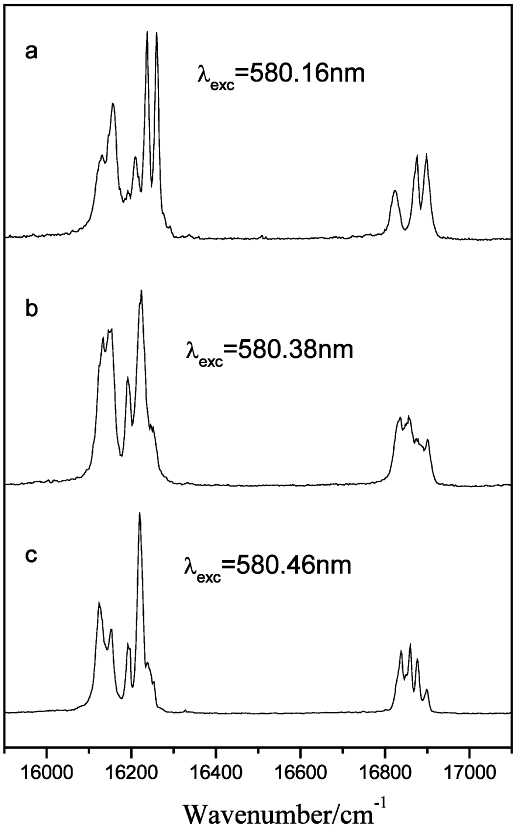

Fig. 7. Emission spectra of complex **1** corresponding to $^5D_0 \rightarrow {}^7F_J (J = 1, 2)$ transitions under selective excitation at 77 K.

hydrogen bonding interactions lead to the stabilization of the crystal.

3.4. Photophysical properties

Fig. 5 illustrates the high-resolution emission spectrum of complex **1** excited with 355 nm at 77 K corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transitions. The intensity ratio of $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1 = 3.64$ shows that the Eu(III) ion is not at an inversion center [16], and that the complex emits red light when exposed to ultraviolet radiation. The number of components of the $^5D_0 \rightarrow {}^7F_1$ transition indicates the presence of more than one chemically different Eu(III) ion sites. The $^5D_0 \rightarrow {}^7F_0$ transition is relatively weak and the emission band is not symmetrical (see insert in Fig. 5). The inhomogeneous broadening of the $^5D_0 \rightarrow {}^7F_0$ emission band arises from the site to site variation in the local field acting on the ions, and has consequently been studied by selective excitation techniques.

The excitation spectra of complex **1** were recorded at 293 K and 77 K setting 16 141 cm^{-1} as the analyzing wavenumber. The excitation bands in Fig. 6(a) are blue-shifted compared with those in Fig. 6(b), which may be due to phonon effect of lattice thermal vibration on energy levels. Fig. 6(a) is comprised of two components labeled A and B with peak positions at 579.9 and 580.16 nm, respectively. This means that there exist two Eu(III) ion sites in complex **1** since $^7F_0$ and $^5D_0$ are non-degenerate, which is in good agreement with the result of X-ray diffraction. The spectrum b determined at 77 K is more resolved than spectrum a, and the peak lines in b are narrower than those in a. It contains a weak broad band C centered at 580.16 nm, and an intense and sharp peak D at 580.46 nm which can be regarded as the bathochromic shift of the peaks A and B of spectrum a. In addition, a shoulder E appears on the short-wavelength side of D with only 0.08 nm difference. Excitation spectra recorded with other analyzing wavenumbers did not reveal any bands positioned at other wavelengths. In order to assign these two $^5D_0 \leftarrow {}^7F_0$ transitions to specific chemical species, we have selectively excited the various $^5D_0$ levels with energies corresponding to the maxima of bands C, E and D [Fig. 7(a)–(c)]. The similarity of Fig. 7(b) and (c) both in the positions and numbers of emission peaks points to the similar Eu^{3+} ion chemical environment when excited at 580.38 and 580.46 nm. But the obvious four peaks in the $^5D_0 \rightarrow {}^7F_1$ transition display that although the emission spectra excited with 580.38 and 580.46 nm are similar, they are still not the same, which shows that the Eu^{3+} ions may have slightly different chemical environments and that the Eu^{3+} ion is very sensitive as a structural probe. Since Fig. 7(a) is significantly different from Fig. 7(b)

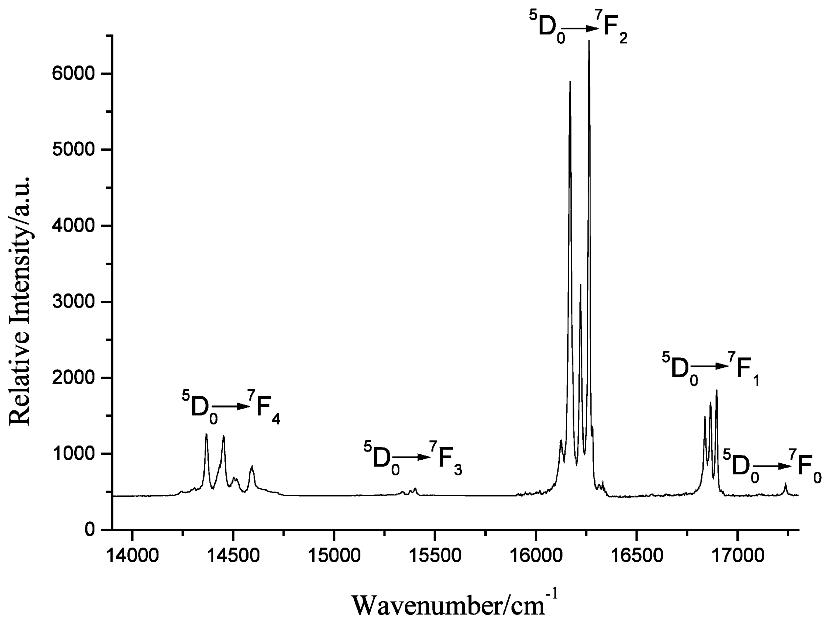

Fig. 8. Emission spectra of complex **2** corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transitions at 77 K, $\lambda_{exc} = 355$ nm.

and (c), undoubtedly, the complex **1** has two Eu^{3+} ion sites.

The average bond distances of Eu–O and Eu–N around Eu1 are 2.454 and 2.608 Å, respectively, which are longer than those around Eu2 (2.448 and 2.583 Å, respectively). So the ionic character of a coordination bond around Eu1 is stronger than that around Eu2. As the Eu1 environment is more ionic, the $^7F_0 \rightarrow {}^5D_0$ transition would be expected to be blue-shifted [17]. Therefore, the site at higher energy 580.16 nm in the excitation spectra can be ascribed to Eu1 for complex **1**, while the one at 580.46 nm can be ascribed to Eu2.

The complex **2** displays a very intense europium(III) luminescence. The emission spectrum of complex **2** at 77 K excited with 355 nm is shown in Fig. 8. The transitions originating from the $^5D_0$ level possess a maximum number of $(2J+1)$ components with 1, 3 and 5 peaks in the range of $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, respectively. The $^5D_0 \rightarrow {}^7F_3$ transition is very weak and the $^5D_0 \rightarrow {}^7F_4$ transition results in overlap of band components. The components of $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–2) transitions may be explained by the europium ion site having a low local symmetry. Its time-resolved spectra can also confirm that there exists only one Eu^{3+} ion site in complex **2** because there is no change in relative intensity or position of peaks with various delay times.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication: CCDC Nos. 177718 and 177719 for **1** and **2**, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work is supported by the National Natural Science Foundation of China (29971005 and 20071004) and a State Key Project of Fundamental Research (G1998061308).

References

[1] (a) B. Benmerad, A.G. Laïdoudi, G. Bernardinelli, F. Balegroune, Acta Crystallogr., Sect. C 56 (2000) 321;
(b) B. Benmerad, A.G. Laïdoudi, F. Balegroune, H. Birkedal, G. Chapuis, Acta Crystallogr., Sect. C 56 (2000) 789;
(c) P.F. Aramendia, R. Baggio, M.T. Garland, M. Perec, Inorg. Chim. Acta 303 (2000) 306;
(d) C. Ünaleroğlu, B. Zümreoğlu-Karan, Y. Zencir, T. Hökelek, Polyhedron 17 (1998) 3979;
(e) K. Binnemans, L. Jongen, C. Bromant, D. Hinz, G. Meyer, Inorg. Chem. 39 (2000) 5938.

[2] (a) L. Pan, E.B. Woodlock, X.T. Wang, C. Zheng, Inorg. Chem. 39 (2000) 4174;
(b) L. Pan, N.W. Zheng, Y.G. Wu, S. Han, R.Y. Yang, X.Y. Huang, J. Li, Inorg. Chem. 40 (2001) 828;
(c) L. Pan, X.Y. Huang, J. Li, Y.G. Wu, N.W. Zheng, Angew. Chem., Int. Ed. Engl. 39 (2000) 527;

(d) T.M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O.M. Yaghi, J. Am. Chem. Soc. 121 (1999) 1651.

[3] (a) E. Galdecka, Z. Galdecki, P. Gawryszewska, J. Legendziewicz, New J. Chem. (1998) 941.;
(b) J.J. Zhao, W.C. Yang, X.Q. Wang, T.Z. Jin, Polyhedron 14 (1995) 2451;
(c) A.Z. Ma, L.M. Li, Y.H. Lin, S.Q. Xi, Acta Crystallogr., Sect. C 49 (1993) 865.

[4] (a) R.Y. Wang, Z.P. Zheng, T.Z. Jin, R.J. Staples, Angew. Chem., Int. Ed. Engl. 38 (1999) 1813;
(b) B.Q. Ma, D.S. Zhang, S. Gao, T.Z. Jin, C.H. Yan, G.X. Xu, Angew. Chem., Int. Ed. Engl. 39 (2000) 3644;
(c) Z.P. Zheng, R.Y. Wang, Comments Inorg. Chem. 22 (2000) 1;
(d) B.Q. Ma, D.S. Zhang, S. Gao, T.Z. Jin, C.H. Yan, New J. Chem. 24 (2000) 251.

[5] A. Mondry, P. Starynowicz, Inorg. Chem. 36 (1997) 1176.

[6] J.-C.G. Bünzli, in: R. Saez-Puche, P. Caro (Eds.), Rare Earths, Editorial Complutense, Madrid, 1998, pp. 223–259.

[7] W.D. Horrocks, Jr., D.R. Sudnick, Acc. Chem. Res. 14 (1981) 384.

[8] A. Panagiotopoulos, T.F. Zafiropoulos, S.P. Perlepes, E. Bakalbassis, I. Massonramade, O. Kahn, A. Terzis, C.P. Raptopoulou, Inorg. Chem. 34 (1995) 4918.

[9] W.M. Lu, B. Wu, L.N. Wang, Y.Q. Lu, Acta Crystallogr., Sect. C 56 (2000) 316.

[10] N. Sabbatin, M. Grardigle, J.-M. Lehn, Coord. Chem. Rev. 13 (1993) 201.

[11] J.G. Kang, S.K. Yoon, Y.K. Sohn, J.G. Kim, Y.D. Kim, I.H. Suh, J. Chem. Soc., Dalton Trans. (1999) 1467.

[12] L.P. Jin, M.Z. Wang, G.L. Cai, S.X. Liu, J.L. Huang, R.F. Wang, Sci. Chin., Ser. B 38 (1995) 1.

[13] F.M. Ramírez, L. Charbonnière, G. Muller, R. Scopelliti, J.-C.G. Bünzli, J. Chem. Soc., Dalton Trans. (2001) 3205.

[14] P.A. Brayshaw, J.-C.G. Bünzli, P. Froidevaux, J.M. Harrowfield, Y. Kim, A.N. Sobolev, Inorg. Chem. 34 (1995) 2068.

[15] G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[16] P. Caro, O.K. Moune, E. Antic-Fidancev, M. Lemaitre-Blaise, J. Less Common Met. 112 (1985) 153.

[17] J. Hölsa, T. Leskelä, M. Leskelä, Inorg. Chem. 24 (1985) 1539.