

A novel photoluminescent and photochromic europium complex

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Abstract A ternary europium complex of 4-aminobutyric acid (ABA) with 1,10-phenanthroline (phen) [Eu₂(ABA)₄(phen)₄](ClO₄)₆ was synthesized and characterized by X-ray single crystal diffraction. The result shows that 4-aminobutyric acid exists in zwitterion form in the binuclear complex and that the carboxylates coordinate with Eu³⁺ ion in bidentate bridging and tridentate chelating-bridging modes. There are two types of phen molecules, one is coordinated and the other is uncoordinated. When excited by YAG : Nd laser with 355 nm light, the title complex can emit strong red fluorescence, and its high-resolution emission spectrum was recorded at 77 K. The Eu³⁺ ion site is in low symmetry, which is in agreement with the result of X-ray single crystal diffraction analysis. When irradiated with a mercury lamp, the aqueous solution of the title complex can perform photochromism with the color change from colorless to green and the green color can fade away in the dark. The photochromic response time is related to the concentration and pH of the solution, the temperature and the light intensity.

Keywords: europium complex, crystal structure, photoluminescence, photochromism, high-resolution spectrum.

The rare earth complexes, especially the europium and the terbium complexes can emit strong fluorescence when irradiated with ultraviolet light. Such complexes have application in the respects of time-resolved immunofluorometric assays, drug analysis, electroluminescent devices, etc.^[1-3]. Therefore, the photoluminescence of rare earth complex has been attractive for many years. Eu³⁺ ion is also a good structural probe^[4]. The relationship between the structure and photoluminescence of the complex can be investigated in the aspects of stationary and the excited state, as well as molecular and local structures.

The study on photochromic substances has been lasting for more than one hundred years since 1867 when Fritsche first found photochromic phenomenon. Recently, it has become the focus of attention due to the prospective application of photochromic materials in optical data storage and optical switching^[5,6]. So far, about twenty categories of photochromic compounds have been found,

among which most are organic compounds, while only a few are complexes. To our knowledge, there are several papers reporting the photochromism of rare earth complexes^[7-9]. But their organic ligand spiropyran itself is photochromic. The rare earth metal ion is not essential to photochromism. We found that the ternary rare earth complexes of amino acid with phen are photochromic, and here the synthesis, crystal structure, photoluminescence and photochromism of the Eu³⁺ complex with 4-aminobutyric acid and phen are reported.

1 Experimental

(i) Reagents and synthesis of the title complex.

4-aminobutyric acid (AR, Sigma) and 1,10-phenanthroline (AR, Beijing Xizhong Chemical Factory) were used. Stock solution of Eu(ClO₄)₃ was prepared by dissolving Eu₂O₃ (99.99%, Guangdong Yangjiang Rare Earth Factory Company Limited) in concentrated HClO₄ and diluted with distilled water to 0.57 mol · L⁻¹.

1 mL aqueous solution of Eu(ClO₄)₃ (0.57 mol · L⁻¹) was added to the ethanolic solution (95%) of 0.176 g 4-aminobutyric acid (1.7 × 10⁻³ mol) and 0.226 g phen · H₂O (1.1 × 10⁻³ mol). The mixture was stirred under reflux for 7 h resulting in a clear solution. After one day, colorless crystals were obtained.

(ii) Determination of crystal structure of the title complex. A colorless prismatic crystal having approximate dimensions of 0.20 mm × 0.20 mm × 0.30 mm was mounted on a glass fiber. All measurements were performed on a Rigaku AFC 7R diffractometer with graphite monochromated Mo-K α radiation (0.071069 nm). The data were collected at a temperature of 293(1) K using the ω -2 θ scan technique. Of the 11434 reflection points collected, 10935 were unique, and 9102 were observed ($I > 3.00\sigma(I)$). The structure was solved by heavy-atom Patterson methods. The crystal data of the title complex are listed as follows: triclinic, space group P $\bar{1}$, $a = 1.3679(2)$, $b = 1.8950(2)$, $c = 1.2997(2)$ nm, $\alpha = 96.21(2)^\circ$, $\beta = 111.22(1)^\circ$, $\gamma = 92.96(2)^\circ$, $V = 3.107(1)$ nm³, $Z = 1$, $D_c = 1.47$ g/cm³, $F(000) = 1396.00$, $R_1(I > 3.00\sigma(I)) = 0.054$, $wR_2(I > 3.00\sigma(I)) = 0.067$. The selected bond distances and bond angles are shown in table 1.

(iii) Determination of the high-resolution fluorescence spectrum of the title complex. The excitation light source was a YAG:Nd laser, which emits at 1.064 μ m, and the excitation wavelength was 355 nm. The sample was placed in a Dewar's bottle and cooled with liquid nitrogen. The fluorescence was collected at right angles through a Spex 1403 high-resolution spectrometer with a photomultiplier tube, then averaged by a Boxcar integrator and finally data were transferred to a computer.

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Table 1 Selected bond distances and bond angles of the title complex^{a)}

Atom	Atom	Distance/nm	Atom	Atom	Distance/nm	Atom	Atom	Distance/nm
Eu	O(1)	0.2356(4)	Eu	O(2)*	0.2370(4)	Eu	O(3)	0.2354(4)
Eu	O(3)*	0.2573(4)	Eu	O(4)*	0.2477(4)	Eu	N(1)	0.2606(6)
Eu	N(2)	0.2637(5)	Eu	N(3)	0.2637(5)	Eu	N(4)	0.2686(5)
Atom	Atom	Atom	Angle/(°)	Atom	Atom	Atom	Angle/(°)	
O(1)	Eu	O(2)*	136.9(1)	O(3)	Eu	N(2)	147.4(2)	
O(1)	Eu	O(3)	77.3(1)	O(3)	Eu	N(3)	88.1(2)	
O(1)	Eu	O(3)*	70.5(1)	O(3)	Eu	N(4)	74.4(2)	
O(1)	Eu	O(4)*	77.0(2)	O(3)*	Eu	O(4)*	50.7(1)	
O(1)	Eu	N(1)	81.8(1)	O(3)*	Eu	N(1)	125.0(1)	
O(1)	Eu	N(2)	134.4(2)	O(3)*	Eu	N(2)	105.9(1)	
O(1)	Eu	N(3)	135.6(1)	O(3)*	Eu	N(3)	144.7(1)	
O(1)	Eu	N(4)	73.7(1)	O(3)*	Eu	N(4)	136.3(1)	
O(2)*	Eu	O(3)	73.6(1)	O(4)*	Eu	N(1)	77.6(2)	
O(2)*	Eu	O(3)*	71.4(1)	O(4)*	Eu	N(2)	68.4(1)	
O(2)*	Eu	O(4)*	94.0(2)	O(4)*	Eu	N(3)	141.7(2)	
O(2)*	Eu	N(1)	137.9(2)	O(4)*	Eu	N(4)	140.2(2)	
O(2)*	Eu	N(2)	75.7(2)	N(1)	Eu	N(2)	62.9(2)	
O(2)*	Eu	N(3)	74.4(2)	N(1)	Eu	N(3)	86.9(2)	
O(2)*	Eu	N(4)	125.8(2)	N(1)	Eu	N(4)	72.1(2)	
O(3)	Eu	O(3)*	74.1(1)	N(2)	Eu	N(3)	73.4(2)	
O(3)	Eu	O(4)*	124.2(1)	N(2)	Eu	N(4)	116.9(2)	
O(3)	Eu	N(1)	144.3(1)	N(3)	Eu	N(4)	62.0(2)	

a) Asterisks indicate symmetry operators X, Y, Z and $-X, -Y, -Z$.

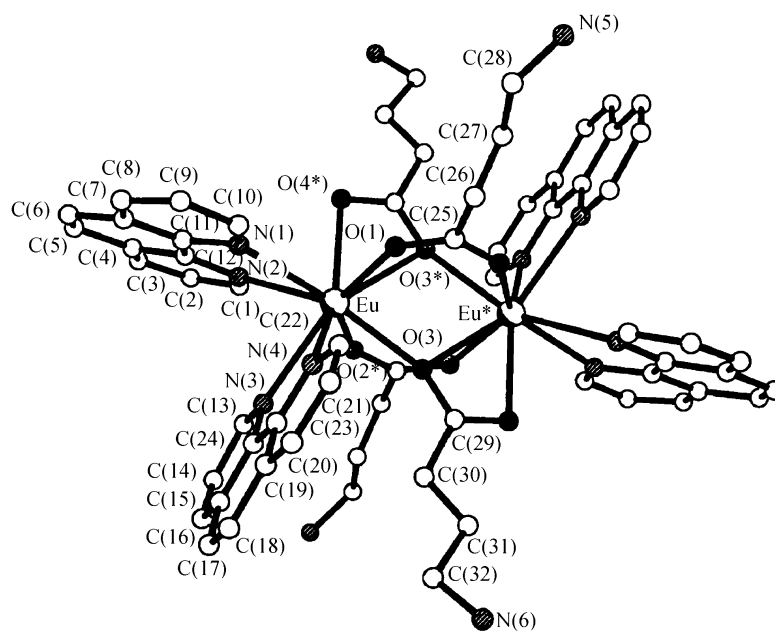


Fig. 1. Molecular structure of the title complex. ClO_4^- , free phen molecules and all hydrogen atoms are omitted for clarity.

(iv) Determination of the UV-Vis spectrum of the title complex. The complex was dissolved in distilled water and diluted to $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ with pH = 6.36. The sample was irradiated by a mercury lamp in a quartz cell for 1 h at 25°C with $E_v = 4.06 \times 10^4 \text{ lux}$, after which its spectral changes were recorded on a Cintra 10e UV-Vis spectrometer, and the time interval is 3 min.

2 Results and discussion

(i) Crystal structure of the title complex. The molecular structure and packing diagram of the complex are shown in figs. 1 and 2, respectively. It can be seen from fig. 1 that the title complex is binuclear. The carboxylates of four 4-aminobutyric acids coordinate with one Eu^{3+} ion in two coordination modes: bidentate bridging and tridentate chelating-bridging. At the same time, every Eu^{3+} ion is also coordinated with two chelated phen molecules leading to the central Eu^{3+} ion nine-fold coordinated. Fig. 2 shows that there exists N—H...N hydrogen bonding between the amino hydrogen atoms of 4-aminobutyric acid and nitrogen atoms of the free phen molecules, and the distance between the two nitrogen atoms is 0.288 nm. The free phen molecules run in a parallel direction with obvious π - π stacking interactions. The distance between the adjacent free phen molecules is 0.274 nm. It is the hydrogen bonding and π - π stacking interactions that stabilize the crystal.

(ii) Photoluminescence of the title complex. The

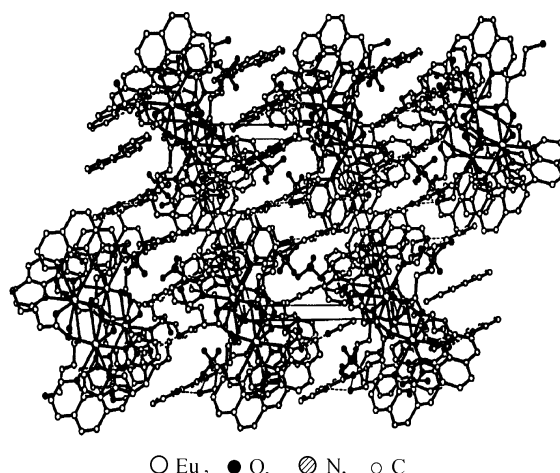


Fig. 2 Cell packing diagram of the title complex in the direction of [010].

high-resolution spectra of the title complex corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($J = 0-4$) transitions of Eu^{3+} ion are given in fig. 3. The obvious 1, 3, 5 emission lines are corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions, respectively. The ratio of the integrated intensity of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ is 2.5, which implies that Eu^{3+} ion site is not located in the symmetric center. Both the composition of the spectra and the ratio of the intensity of 0-2 and 0-1 transitions show that the Eu^{3+} ion site is in low symmetry^[4], which is in good agreement

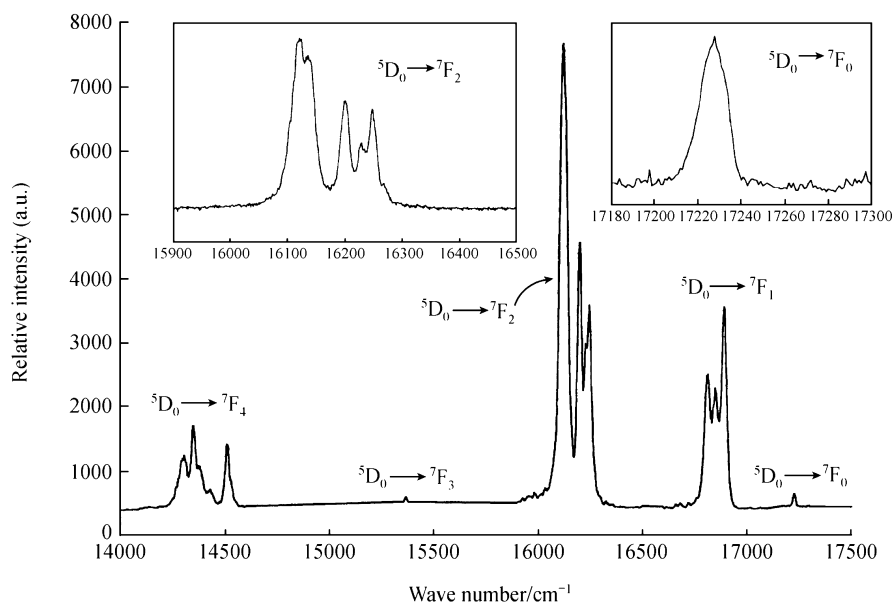


Fig. 3. High-resolution spectra of the title complex corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($J = 0-4$) transitions.

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with the result of crystal structure analysis. The inserted figures in fig. 3 give the enlarged spectra of $^5D_0 \rightarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_2$ transitions, respectively. The spectrum corresponding to $^5D_0 \rightarrow ^7F_0$ transition is not completely symmetrical. The hypersensitive transition $^5D_0 \rightarrow ^7F_2$ is readily affected by the coordination environment. Both the Stark components and the shoulder in the main peaks show that the two Eu^{3+} ions are located in a little different chemical environment in the binuclear complex^[4].

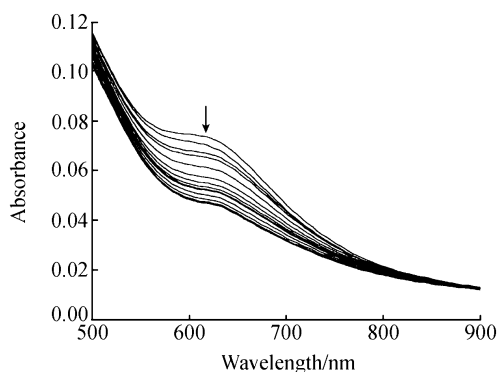


Fig. 4. Spectral changes of the green solution in the decoloration process.

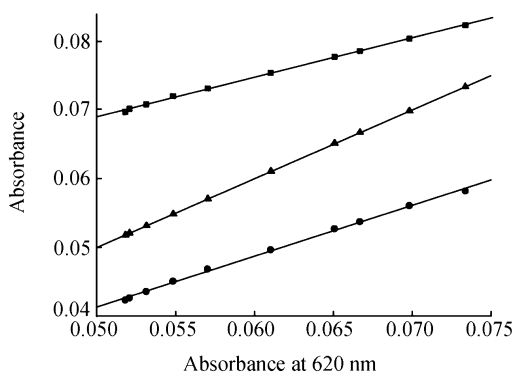


Fig. 5. E-diagram of fig. 4, the absorbance at 620 nm is plotted against those at 550 (■), 620 (▲) and 670 nm (●).

(iii) Photochromism of the title complex. By irradiating the aqueous solution of the title complex with a mercury lamp, the solution would become green from colorless. The spectral changes of the title complex in aqueous solution after mercury lamp irradiation for 1 h are given in fig. 4. It can be seen from fig. 4 that a wide band centered at 620 nm appears when the solution turns green. The green color will fade away after 0.5 h in the dark with the absorption at 620 nm disappearing. This process is

reversible for many times. Its E-diagram (fig. 5) can be obtained with the absorbance at 620 nm plotted against those at 550, 620 and 670 nm. The linear relationship in fig. 5 shows that only one independent step is involved in the decoloration process. The results show that the concentration, pH of the solution, temperature and the irradiation time can affect the photochromism. Higher pH (<7), higher concentration, longer-time irradiation and lower temperature will make photochromism response rapidly.

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